A TECHNICAL AND ECONOMIC ASSESSMENT OF THE REACTIVITY OF SASKATCHEWAN LIGNITE COALS AS THEY RELATE TO GASIFICATION PROCESSES PHASE IV

Final Report

by

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EXECUTIVE SUMMARY

The catalytic effects of calcium and sodium in steam gasification of Saskatchewan lignite chars has been elucidated. Lignite reactivity was determined using chars derived from run-of-mine (ROM) lignite, chars derived from lignite demineralized with hydrochloric acid, and chars derived from lignite enriched with controllable amounts of calcium and sodium.

The results show that the reactivity of demineralized chars was significantly reduced as compared to the reactivity of corresponding ROM or ion-exchanged lignite chars. The catalytic effect of calcium and sodium in the steam gasification of lignite chars was found to be similar when the cation concentration was expressed on a mole/gram of fixed carbon basis.

Correlation between enriched lignite sodium or calcium concentration and steam gasification char reactivity provided a good approximation of ROM char gasification behaviour. Analysis of char gasification behaviour in both steam and steam/air atmospheres was most accurately and conveniently performed using the method based on a dimensionless time parameter.

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INTRODUCTION

In order to improve the efficiency of energy conversion and increase the CO/CO_2 ratio of the product gas in gasification processes, it is desirable to lower the temperature of steam gasification of coal chars. For this purpose catalysts can be used, provided their addition can be performed in an economical manner. In lignites such a catalyst is provided by nature in the form of iron and alkali metals present in lignite mineral matter and in alkali salts of lignite acidic functional groups.

Alkali metals are known to catalyze carbon gasification reactions in steam and steam/oxygen atmospheres, whereas transition metals such as iron require the presence of reducing conditions. Both conditions prevail during air/steam gasification in which part of the steam and oxygen have reacted to form hydrogen and carbon monoxide.

The possible catalytic influence of coal minerals on the steam gasification reaction has been the subject of many studies. Calcium salts have been shown by some investigators to provide a relatively higher increase in gasification reactivity in comparison to other alkali metal salts (Taylor and Neville, 1921; Haynes et al., 1974; Wilks, 1976), whereas other researchers have reported calcium to be totally ineffective (Kayembe and Pulsifier, 1976). The catalytic reactivity of calcium was demonstrated by Otto et al. (1979) using thermogravimetric methods; however, Huettinger and Krauss (1982) failed to reproduce these findings in their fixed bed flow reactor. Lang and Neavel (1982) showed that calcium compounds provide good catalytic activity only under certain conditions.

They concluded that the calcium must be essentially atomically dispersed throughout the char in order to obtain adequate catalyst activity.

Such a dispersion can be obtained when the catalyst is transferred to acid sites in coal by ion-exchange. In low rank coals, there are a sufficient number of active sites due to naturally occurring ion exchange with calcium. Hence, lignitic coals should demonstrate a high degree of reactivity during gasification in steam atmospheres.

The work presented here includes the results of an investigation of the catalytic effect of calcium and sodium on the steam and steam/air gasification of Saskatchewan lignite. In order to study and obtain a quantitative measure of their effect, tests were conducted on lignite chars derived from ROM lignites, chars derived from lignite demineralized with 2N hydrochloric acid to remove exchangeable cations, and lignite chars derived from acid-washed coals enriched with various amounts of sodium and calcium cations using sodium and calcium acetate exchange solutions. The ROM and treated lignites were carbonized and gasified in a fixed-bed reactor.

EXPERIMENTAL

Preparation of Acid-Washed and Ion-Exchanged Lignite Coals

Estevan and Coronach lignites were air-dried, ground and then sieved to provide representative samples with a particle size range of 1.0-2.4 mm. Acid-washed (cation-free) coals were prepared from ROM lignites by extraction with 2N HCl at 60°C. After extraction the cation-free coals were washed with water at 60°C until the filtrate was chloride-free, and then dried under nitrogen at 105°C.

Lignites with various calcium or sodium contents were prepared from the acid-washed coals by treatment with 0.5 N, 1 N and 2 N calcium and sodium acetate solutions. The 2 N sodium acetate solution contained 3.6 N NaOH in order to maintain a sufficiently high pH. The ion-exchanged coals were then washed with cold water to remove any excess acetates, and subsequently dried under nitrogen at 105°C. The proximate and ultimate analyses of the ROM and prepared lignite samples are presented in Tables 1 and 2.

Preparation of Chars from Untreated, Acid-Washed and Ion-Exchanged Coals

Chars from ROM and treated coals were prepared in a fixed bed reactor under an atmosphere of flowing nitrogen, with a heat-up rate of 4°C/min. The samples were "soaked" for a one hour time period, with continued flow of nitrogen, once a bed temperature of 25°C below the designated gasification temperature was obtained. Following this carbonization

Table 1. PROXIMATE ANALYSIS OF ROM, ACID-WASHED AND ION-EXCHANGED COALS

Coal Type	Moisture* (%)	Ash (%)(Dry)	Volatiles (%)(Dry)	Fixed Carbon** (%)(Dry)
		Coronach		
Untreated	5.47	11.78	44.30	43.92
Acid-Washed	2.34	3.00	46.53	50.47
Sodium Exchanged				
Na(A)	0.76	10.05	43.84	46.11
Na(B)	1.73	9.16	43.28	47.56
Na(C)	0.32	5.61	43.21	51.18
Calcium Exchanged				
Ca(A)	4.86	5.25	49.14	45.61
Ca(B)	1.48	3.52	50.85	45.63
Ca(C)	3.56	4.26	49.84	45.90
		Estevan		
Untreated	5.27	12.43	40.92	46.65
Acid-Washed	4.89	4.38	42.43	53.19
Sodium Exchanged				
Na(A)	0.99	10.62	39.94	49.44
Na(B)	3.99	12.89	39.64	47.47
Na(C)	1.82	6.94	41.39	51.67
Calcium Exchanged				
Ca(A)	2.15	9.85	44.13	46.02
Ca(B)	1.52	4.09	47.71	48.20
Ca(C)	1.69	6.38	44.44	49.18

*After drying under nitrogen.
**% Fixed Carbon = 100 - (% ash + % volatile).

Table 2. ULTIMATE ANALYSIS OF ROM, ACID-WASHED AND ION-EXCHANGED COALS

Coal Type	Carbon (%)	Hydrogen (%)	Nitrogen (%)	Cation Concentration (mole/g FC) X 10^3 Ca^{2+}	Na^+
		Coronach			
Untreated	58.49	3.80	0.77	1.1	0.2
Acid-Washed	65.73	4.32	0.87	0	0
Sodium Exchanged					
Na(A)	62.41	4.00	0.76	0	3.2
Na(B)	62.61	4.22	0.78	0	2.7
Na(C)	65.30	4.31	0.82	0	1.0
Calcium Exchanged					
Ca(A)	63.73	4.24	0.77	2.1	0
Ca(B)	64.36	4.36	1.17	0.7	0
Ca(C)	65.11	4.32	0.74	1.0	0
		Estevan			
Untreated	63.26	4.07	1.24	0.9	0.4
Acid-Washed	63.31	4.13	1.23	0	0
Sodium Exchanged					
Na(A)	63.79	4.05	1.13	0	2.9
Na(B)	61.29	3.92	1.09	0	2.9
Na(C)	66.24	4.29	1.15	0	1.0
Calcium Exchanged					
Ca(A)	62.55	4.14	1.07	1.3	0
Ca(B)	65.75	4.38	1.14	0.9	0
Ca(C)	64.52	4.27	1.11	1.0	0

procedure, the resultant chars were gasified with steam or steam/air reactant mixtures.

The numbering system used for the identification of coals and gasification conditions is explained in Table 3.

Apparatus and Gasification Procedure

A detailed description of the equipment and experimental procedure used in previous work as well as in this phase of the program was presented elsewhere (Van Der Heijden et al., 1982). For clarity, however, a brief description of the equipment is given here.

The fixed bed reactor consists of a 1525 mm long Hastelloy C-276 cylinder with an ID of 51 mm (Figure 1). The reactor is heated with an external 6 kW electrical furnace. Coal is introduced from the top of the reactor and supported by a perforated carbon steel disc. Devolatilization products produced during the carbonization step are quenched and exhausted outside through a ball valve attached to the uppermost flange of the reactor. After carbonization this ball valve is closed in order that the reactor vessel may be pressurized. The gasification products exit the reactor approximately 15 cm from the top and flow through the gas letdown and sampling lines.

The off gases are quenched and filtered to remove tars and condensible hydrocarbons and reduced to atmospheric pressure. A wet test meter was used to measure the total gas volume. The outlet of the test meter is connected to a manifold attached to two Riken (model RI-550A)

REACTANT GAS MIXTURE	PRESSURE MPa	CHAR TYPE									
		ROM		ACID-WASHED		Na(A)	Na(B)	Na(C)	Ca(A)	Ca(B)	Ca(C)
		TEMPERATURE, °C									
		800	900	800	900	800	800	800	800	800	800
STEAM/AIR	0.1	C1	C2	C7	C8						
		E1	E2	E7	E8						
	2.0	C3	C4	C9	C10						
		E3	E4	E9	E10						
STEAM	2.0	C5	C6	C11	C12	C13	C14	C15	C16	C17	C18
		E5	E6	E11	E12	E13	E14	E15	E16	E17	E18

C = Coronach lignite
E = Estevan lignite

Table 3. SAMPLE AND RUN IDENTIFICATION SYSTEM

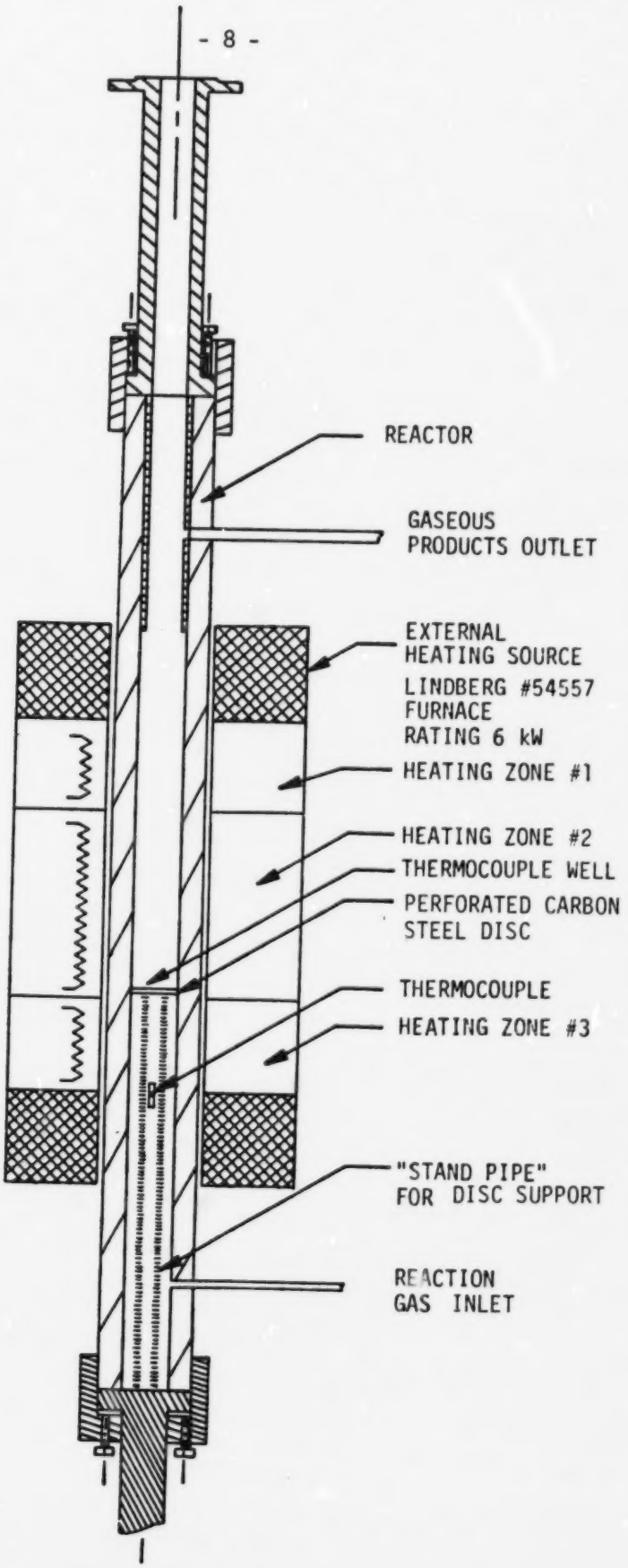

Figure 1. FIXED BED REACTOR CONFIGURATION

non-dispersive infrared gas analyzers which measure the concentrations of carbon monoxide and carbon dioxide in the off-gas. The reactant gas mixtures, consisting of steam/air or steam/nitrogen, were introduced into the reactor below the perforated disc supporting the coal char. A diagram of the experimental set-up is presented in Figure 2.

The reactor was pressurized to the desired operating pressure with nitrogen, following carbonization and the specified reactant mixture was introduced to the reactor. During gasification of the char, CO and CO_2 concentrations in the gas and cumulative gas production were measured at two-minute intervals. The CH_4 concentration was monitored only during selected experiments because of the low concentration of the component in the gas.

Gasification runs were considered complete when the off-gas flowrate dropped below 7 L/min and/or both CO and CO_2 concentrations in the product gas dropped below one percent by volume. All runs were terminated by stopping all gas flows, and allowing the reactor to cool overnight. The reactor was then depressurized and residual char/ash removed for analysis.

Similar procedures were followed for gasification runs at 0.1 MPa as 2 MPa pressure. The amount of carbon at the start of gasification was calculated from the carbon remaining in the char/ash residue and the amount of CO and CO_2 produced during gasification.

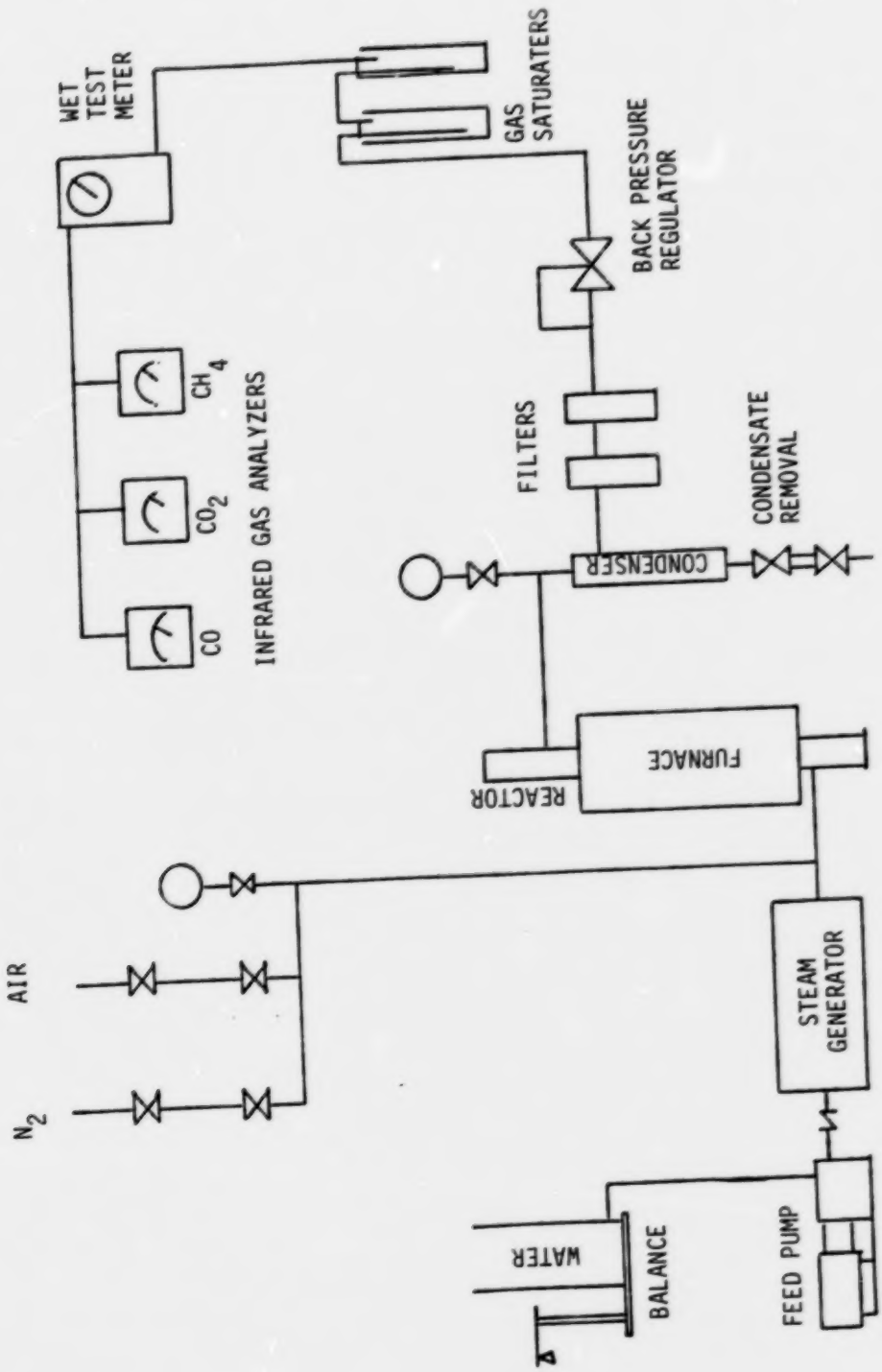

Figure 2. EXPERIMENTAL SETUP

RESULTS AND DISCUSSION

General

Throughout this work coal reactivity is defined by an apparent rate constant, k', calculated from the conversion of carbon to carbon oxides following first order kinetics for steam gasification and zero order kinetics for steam/air gasification. The value of k' could not be determined directly from the initial steam-carbon reaction rate and it had to be obtained from integrated conversion *vs.* time relationships. As an alternative approach a half-life time is also used to reflect the reactivity of lignite chars.

The rate of carbon conversion in steam gasification increases at fractional conversions less than 0.2 (Figure 3) and, therefore, the rate is not amenable to analysis at the initial conditions. It has been decided therefore, that k' would be determined from a simple plot of $-\ln(1 - X)$ *vs.* reaction time (where X is the fractional carbon conversion) since both the reaction rate and integrated carbon conversion are well correlated by first order kinetics, in steam-only atmospheres, within the fractional conversion range of 0.2 to 0.8 (Figure 4). This approach yields generalized correlations for lignite char reactivities which are good approximations to actual gasification behaviour, as shown in the following sections.

In the experimental portion of this work, the ROM and treated coals were charred and subsequently gasified without removal from the gasifier. Hence, the exact amount of char present at the start of gasification is not

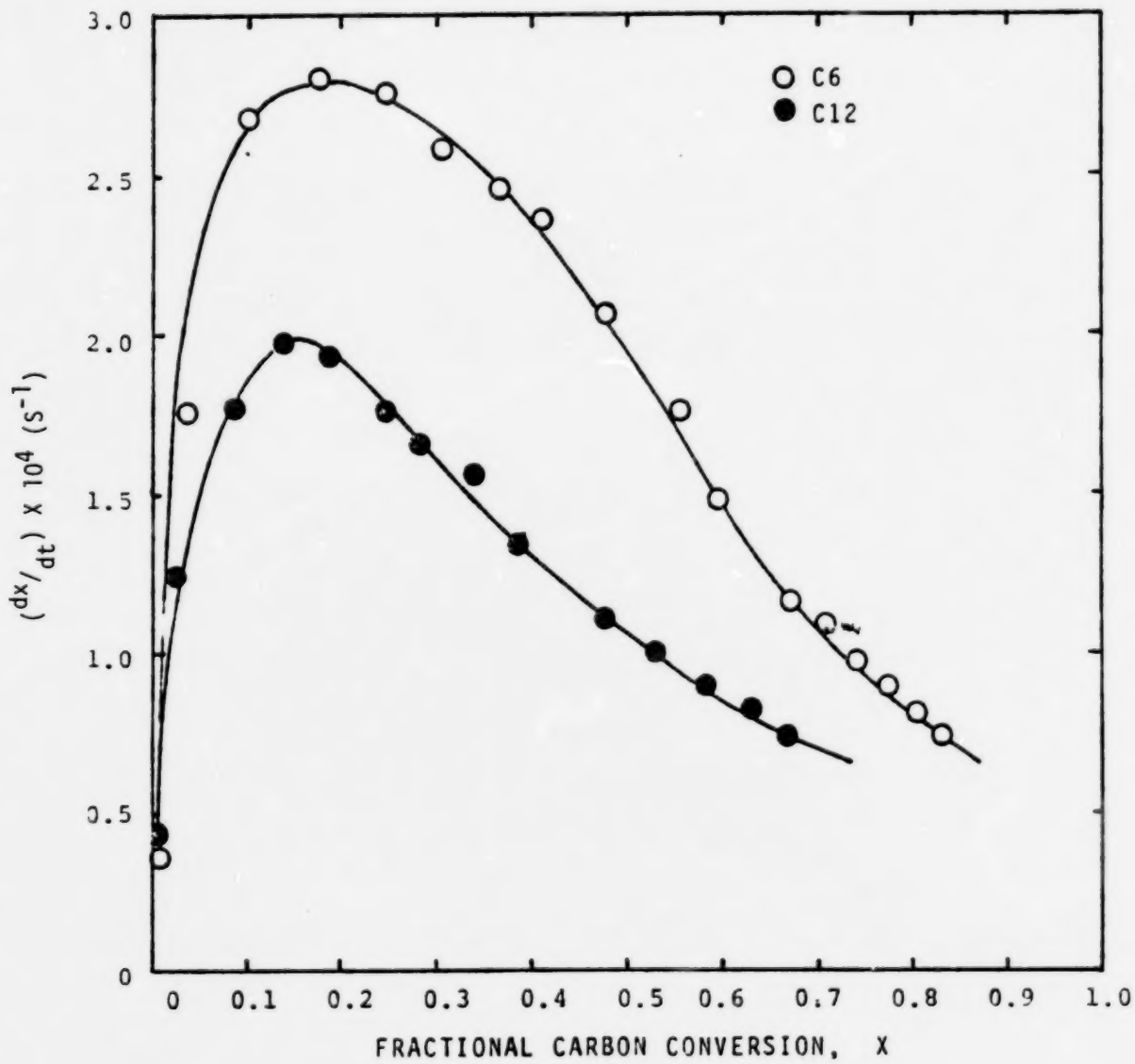

Figure 3. VARIATION OF REACTION RATES DURING STEAM GASIFICATION OF ROM AND ACID-WASHED CHARS AT 900°C AND 2 MPa

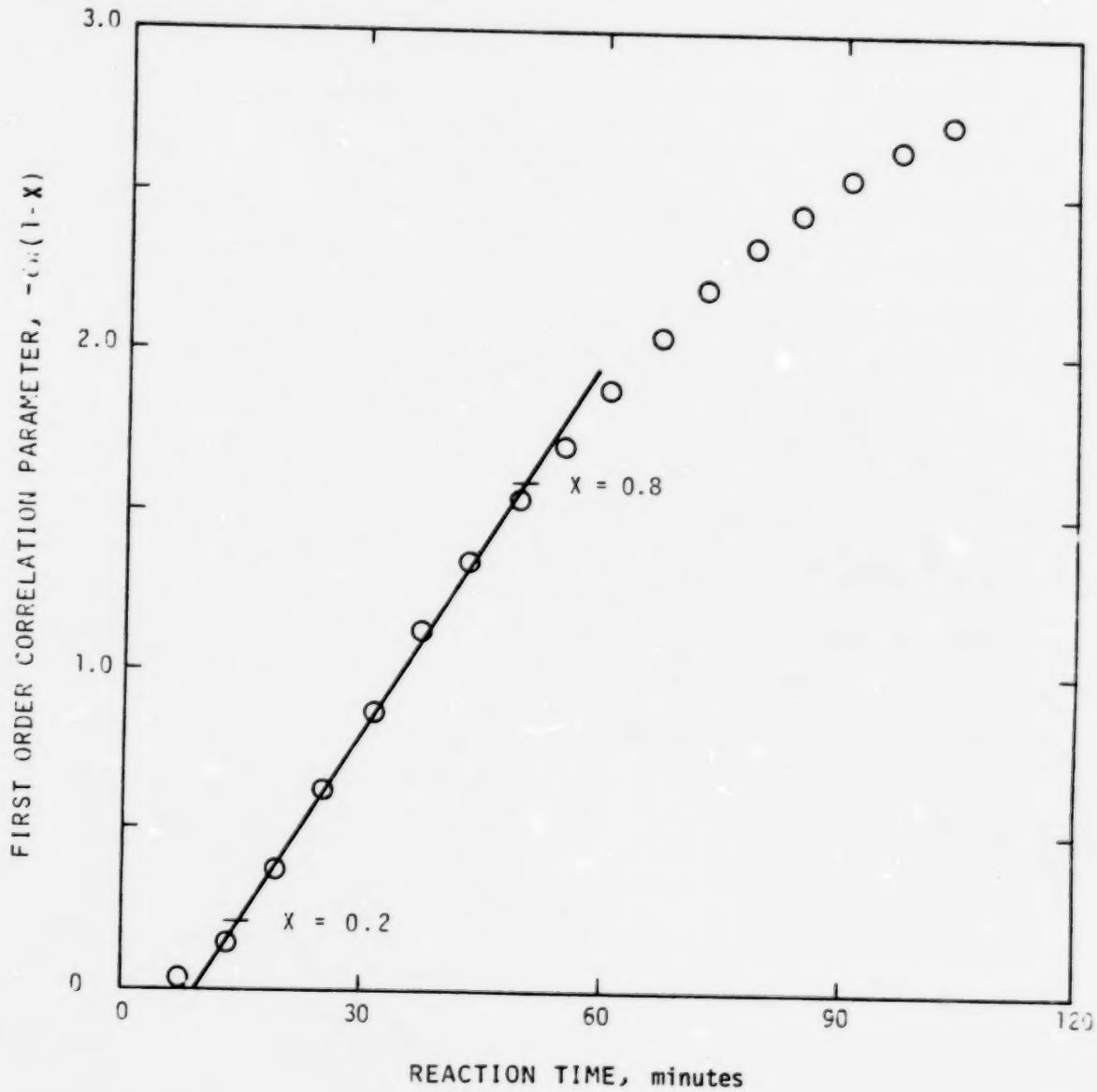

Figure 4. FIRST ORDER KINETICS FOR GASIFICATION OF C14 CHAR IN STEAM

known and has to be obtained in an indirect manner. An assumption is made that the total amount of carbon in the char is the sum of the carbon remaining in the char/ash residue at the end of the run and the total amount of carbon in the product gas in the form of CO and CO_2. An assumption that the amount of carbon in the char at the start of gasification corresponds to the amount of fixed carbon in the parent ROM or treated lignites, as determined from proximate analysis, has proven to be invalid. In all cases, the total carbon as calculated from proximate analysis was 20 to 80 percent above the total carbon determined from the mass balance (i.e., carbon in ash + carbon in gas). Proximate and ultimate analyses of char/ash residues are presented in Tables 4 and 5.

A plausible explanation of this difference is that coal fines are carried over with the nitrogen stream during the carbonization of the coals. Both the acid-washed and ion-exchanged coals show, in general, greater "losses" than the ROM coals. However, the possibility that this loss is due to cation addition was discarded on the basis of the study by Tyler and Schafer (1980). Their work showed that addition of Ca^{++} to a cation-free coal decreased the yields of tar and total volatile matter, while removal of cations markedly increased the yield of tar and volatile matter. Reduction in the flowrate of nitrogen during charring, in some runs, resulted in a reduction of these losses, further confirming that this loss is mainly due to carryover of carbon during the carbonization step.

In steam gasification the main gaseous products are, CO, CO_2, and H_2 although some CH_4 has been detected in gaseous reaction products, even where pure carbon is gasified with steam. It is not certain whether this

Table 4. PROXIMATE ANALYSIS OF GASIFIED CHAR/ASH RESIDUES

Sample	Type	Moisture (%)	Ash (%)(Dry)	Volatiles (%)(Dry)	Fixed Carbon* (%)(Dry)
			Coronach		
C1	Untreated	0.12	99.3	1.0	0
C2	Untreated	0.72	99.5	1.1	0
C3	Untreated	0.51	99.7	0	0.3
C4	Untreated	0.18	100.0	0	0
C5	Untreated	1.37	91.0	9.0	0
C6	Untreated	0.80	99.8	0.1	0.1
C7	A-W	2.45	49.5	16.5	34.0
C8	A-W	0.98	56.0	11.0	33.0
C9	A-W	1.28	65.7	19.2	15.1
C10	A-W	1.00	77.3	13.1	9.6
C11	A-W	0.11	32.4	6.8	60.8
C12	A-W	0.24	89.4	9.2	1.4
C13	Na(A)	0.24	88.7	5.5	5.8
C14	Na(B)	1.20	98.1	2.2	0
C15	Na(C)	0.27	95.2	5.5	0
C16	Ca(A)	0.47	87.5	9.3	3.2
C17	Ca(B)	0.17	96.8	4.2	0
C18	Ca(C)	0.10	88.8	10.4	0.8
			Estevan		
E1	Untreated	0.08	99.8	0.6	0
E2	Untreated	0.13	97.5	2.6	0
E3	Untreated	0.05	99.8	0.5	0
E4	Untreated	0.23	100.0	0.1	0
E5	Untreated	0.79	92.4	8.3	0
E6	Untreated	0.52	99.3	0.1	0.6
E7	A-W	1.15	74.2	23.5	2.3
E8	A-W	6.29	45.5	15.4	39.1
E9	A-W	0.12	96.5	3.5	0
E10	A-W	0.02	99.4	0.9	9.4
E11	A-W	0.65	51.1	10.1	38.8
E12	A-W	0.37	79.5	5.5	15.0
E13	Na(A)	0.76	92.5	8.7	0
E14	Na(B)	0.86	86.6	4.2	0
E15	Na(C)	0.47	69.5	16.2	14.3
E16	Ca(A)	0.68	68.5	10.7	20.8
E17	Ca(B)	0.53	88.1	9.7	2.2
E18	Ca(C)	0.30	78.1	11.2	10.7

*% Fixed Carbon = 100 - (% ash + % volatile).

Table 5. ULTIMATE ANALYSIS OF GASIFIED CHAR/ASH RESIDUES

Sample	Type	Carbon (%)	Hydrogen (%)	Nitrogen (%)
		Coronach		
C1	Untreated	0.46	0.06	0.03
C2	Untreated	0.94	0.06	0.02
C3	Untreated	0.16	0.04	0.03
C4	Untreated	0.45	0.04	0.01
C5	Untreated	6.01	0.30	0.03
C6	Untreated	1.08	0.11	0.06
C7	A-W	30.67	0.50	0.96
C8	A-W	31.61	1.56	1.15
C9	A-W	35.60	2.52	2.37
C10	A-W	22.78	1.44	3.00
C11	A-W	64.19	0.58	0.08
C12	A-W	13.81	0.57	0.03
C13	Na(A)	6.62	0.70	0.08
C14	Na(B)	3.95	0.43	0.02
C15	Na(C)	10.67	0.69	0.24
C16	Ca(A)	11.60	0.41	0.15
C17	Ca(B)	8.45	0.14	0.02
C18	Ca(C)	14.38	0.26	0.09
		Estevan		
E1	Untreated	0.41	0.03	0.01
E2	Untreated	1.23	0.16	0.03
E3	Untreated	0.27	0.04	0.01
E4	Untreated	0.45	0.06	0
E5	Untreated	5.39	0.24	0.01
E6	Untreated	0.75	0.07	0
E7	A-W	24.09	1.76	0.57
E8	A-W	37.02	0.70	0.48
E9	A-W	2.61	0.13	0.18
E10	A-W	1.61	0.05	0.01
E11	A-W	42.94	0.58	0.37
E12	A-W	24.37	0.27	0.08
E13	Na(A)	8.43	0.51	0.33
E14	Na(B)	28.76	0.40	0.13
E15	Na(C)	28.76	0.40	0.13
E16	Ca(A)	35.25	0.31	0.18
E17	Ca(B)	15.68	0.34	0.10
E18	Ca(C)	21.49	0.24	0.08

methane results from the direct reaction of steam with carbon or from the secondary reaction of hydrogen, produced from the steam-carbon reaction, with the carbon in the char. Nevertheless, the total amount of methane produced during gasification with steam is negligible in terms of the total amount of carbon converted into CO and CO_2 gaseous products. A plot of the typical volume fractions of CO, CO_2 and CH_4 produced over the duration of a steam gasification run is presented in Figure 5.

Steam Gasification of Chars Derived from Untreated, Acid-Washed and Ion-Exchanged Coals

The analysis of steam gasification kinetics was performed using two theoretical methods. The first method was based on a detailed calculation of an apparent rate constant, k', for each gasification run. In the second method, the conversion of carbon was plotted *vs.* dimensionless time, τ, defined in terms of the time required to gasify half of the initial carbon in the char.

Initially, two rate expressions were used in detailed calculations of rate constants. A first order rate expression (1):

$$\text{Rate} = k'(1 - X) \qquad (1)$$

(where X is the fractional carbon conversion) which gives the integrated equation (2):

$$I(X) = -\ln(1 - X) = k't \qquad (2)$$

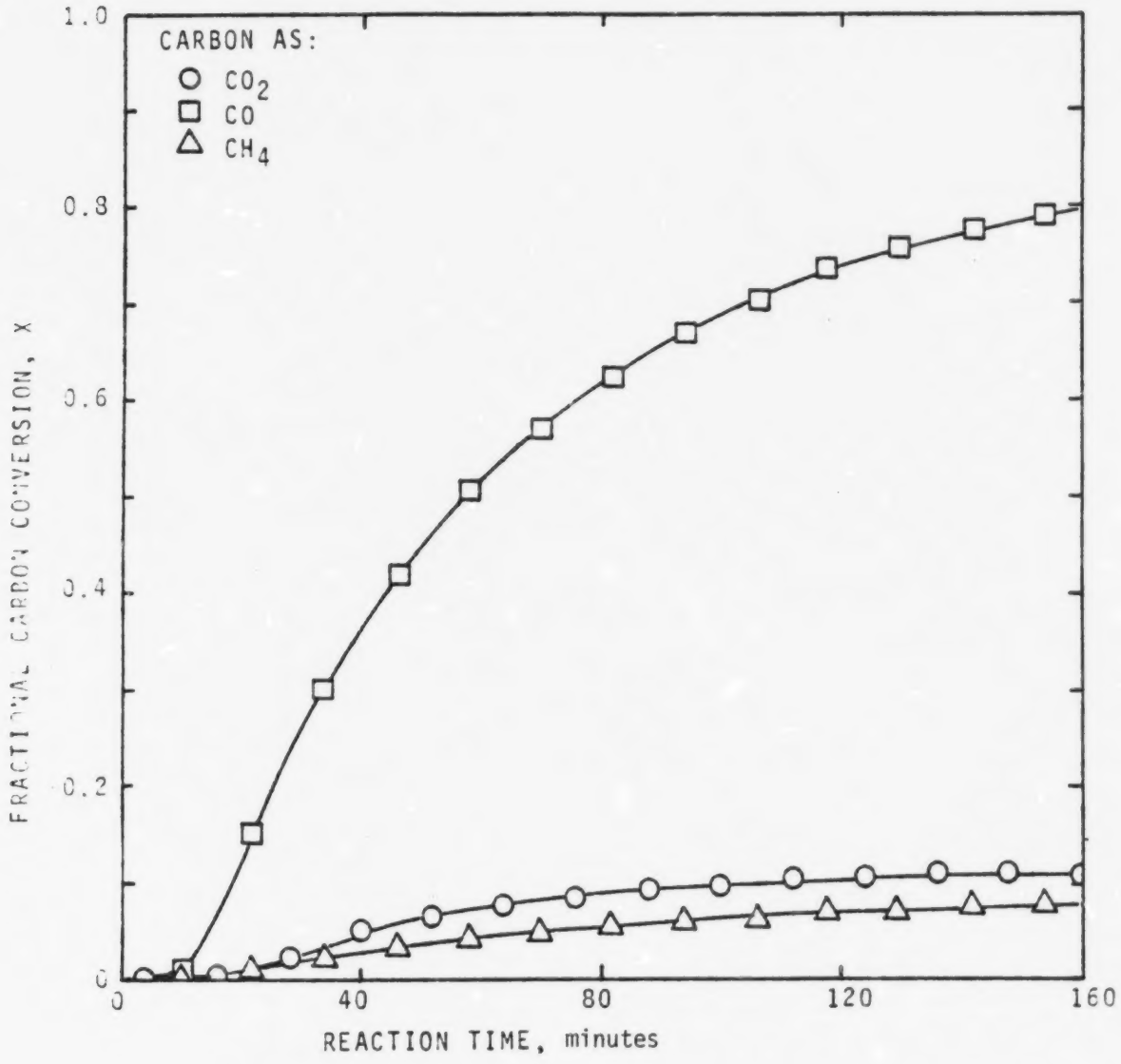

Figure 5. FRACTIONAL CARBON CONVERSION OF C6 CHAR IN STEAM AS CO_2, CO and CH_4

and a fractional order rate expression (3):

$$\text{rate} = k''(1 - X)^{2/3} \exp(-\alpha X^2) \qquad (3)$$

where α is a kinetic parameter dependent on gas composition and pressure.

For gasification in steam only atmospheres $\alpha = 0$. Reference using this value in equation (3) the following integration rate expression (4) results:

$$I(X) = 3[1 - (1 - X)^{1/3}] = k''t \qquad (4)$$

Equations (2) and (4) were then tested for correlating carbon conversion data by plotting I(X) functions vs. conversion time (Figure 6). Both rate expressions gave a good fit to experimental data for fractional conversion of carbon less than 0.5. At higher conversions, equation (4) resulted in poor correlation, indicating that k" became a function of carbon conversion. Equation (4), therefore, was discarded and the rate constants, k', based on the first order expression (2), were used as a measure of char reactivity.

Table 6 presents k' values for ROM and treated lignite chars. In all cases, sodium- and calcium-treated lignites show higher reactivities than acid-washed lignites. The ROM lignites show higher reactivities, also, due to naturally occurring concentrations of alkali metals in the form of the salts of acidic functional groups.

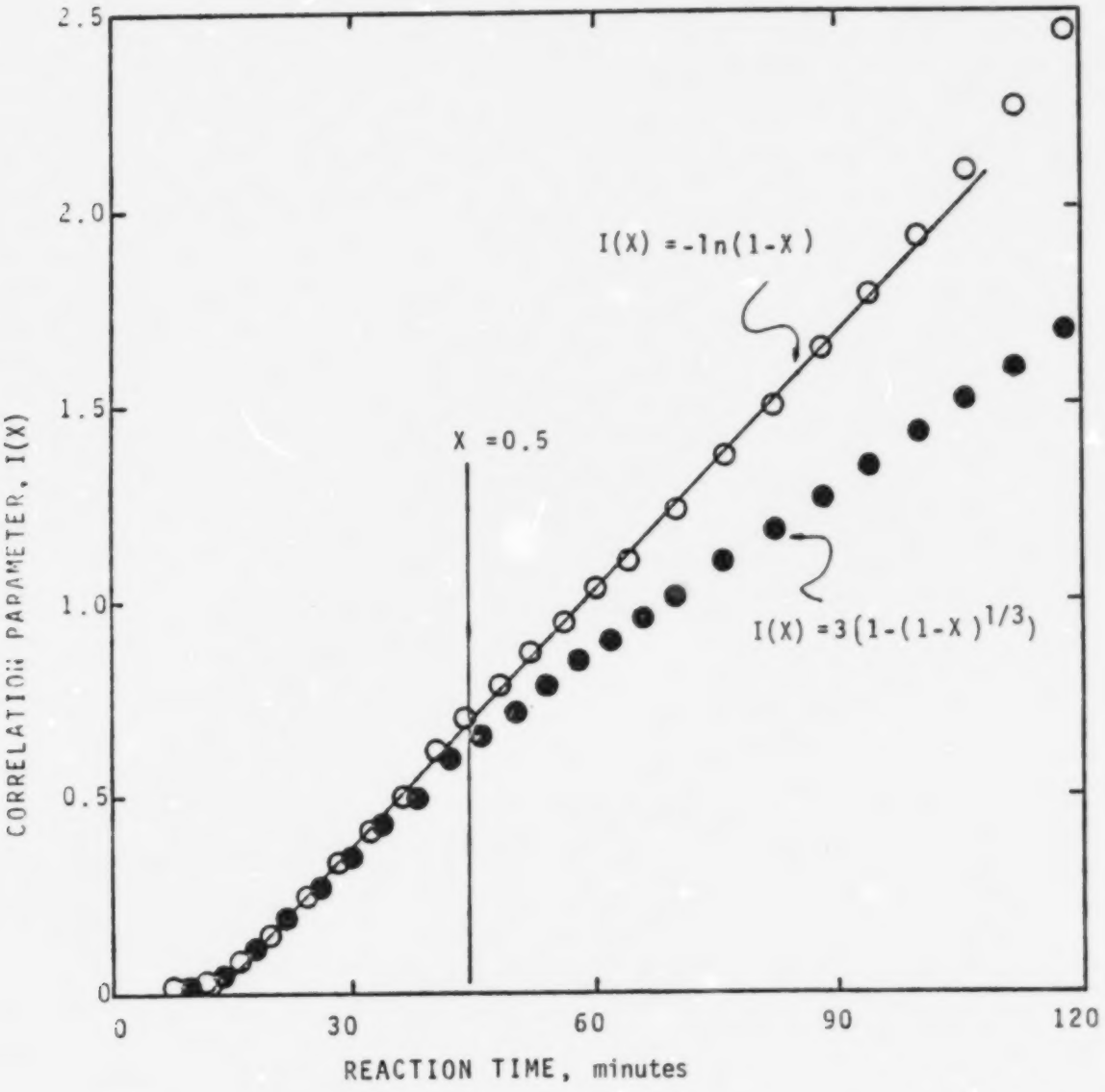

Figure 6. COMPARISON BETWEEN FIRST AND FRACTIONAL ORDER CORRELATION PARAMETERS FOR THE STEAM GASIFICATION OF C6 CHAR

Table 6. KINETIC PARAMETERS FOR THE STEAM GASIFICATION OF ROM AND TREATED CHARS AT 2 MPa

Sample	Type*	Temperature (°C)	$k' \times 10^2$ (min^{-1})
		Coronach	
C5	ROM	800	1.325
C6	ROM	900	1.989
C11	A-W	800	0.732
C12	A-W	900	1.280
C13	Na(A)	800	3.456
C14	Na(B)	800	4.201
C15	Na(C)	800	2.484
C16	Ca(A)	800	1.889
C17	Ca(B)	800	1.517
C18	Ca(C)	800	1.593
		Estevan	
E5	ROM	800	1.673
E6	ROM	900	3.629
E11	A-W	800	0.644
E12	A-W	900	1.355
E13	Na(A)	800	3.067
E14	Na(B)	800	2.634
E15	Na(C)	800	1.000
E16	Ca(A)	800	2.065
E17	Ca(B)	800	1.519
E18	Ca(C)	800	1.657

* For values of Na(A), Na(B) and Ca(A), etc. see Table 2.

On the other hand, similar reactivities for all acid-washed samples suggested that, for lignites from the same geological deposits, the catalytic effect of alkali metals could be treated as if it were independent of the lignite organic matrix. In order to test this hypothesis, reactivity ratios defined by $k'_{treated}/k'_{acid\text{-}washed}$ were plotted *vs.* the concentrations of sodium and calcium in treated lignites (Figure 7). The least squares fit of the reactivity ratios gave the following regression equation (5):

$$k'/k'_o = 1.16 + 1.24(Y) \times 10^3 \qquad (5)$$

where Y = concentration of calcium and sodium in moles/g fixed carbon and k'_o = rate constant for acid-washed lignite.

Equation (5) correlates the reactivity ratio and the alkali metal concentration of the lignites with the following statistical coefficients:

R^2 = regression coefficient = 0.81

and

$$\alpha = 0.17$$

To further test equation (5), conversion data for Estevan and Coronach lignites were compared with theoretical conversions, based on k' values calculated from equation (5) and the analysis of ROM lignites (Table 7). In both cases (Figures 8 and 9) predicted conversion were 5 to 20%,

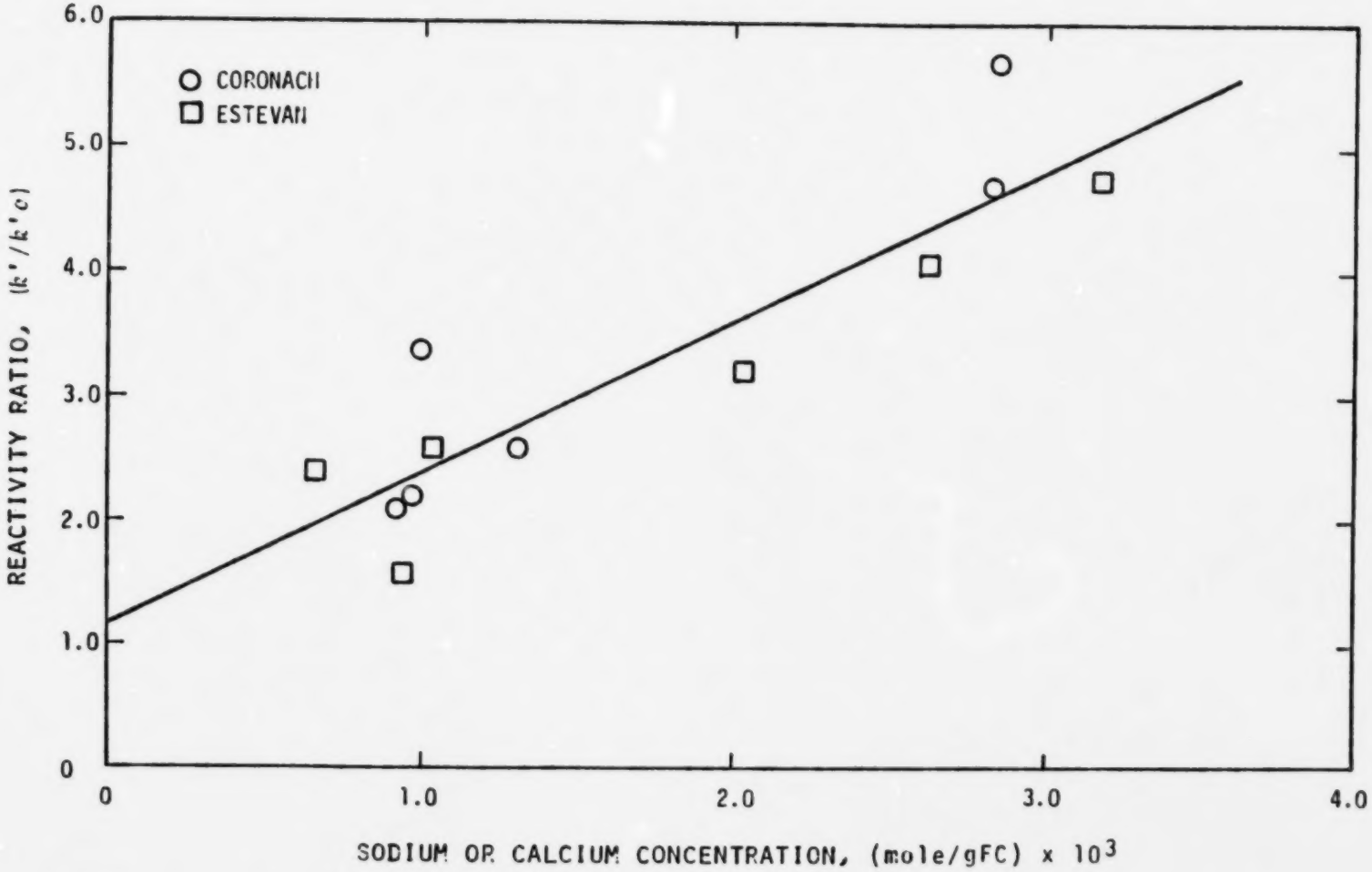

Figure 7. EFFECT OF SODIUM OR CALCIUM CONCENTRATION ON THE REACTIVITY OF ENRICHED LIGNITE CHARS GASIFIED IN STEAM AT 800°C AND 2 MPa

Table 7. REACTIVITY RATIOS FOR Ca^{++} AND Na^{+} ENRICHED CHAR GASIFICATION IN STEAM AT 800°C and 2MPa

Sample	Cation Concentration (mole/g FC)X10^3 Y_{Ca}	Y_{Na}	Reactivity Ratio
C5	1.26*		1.81
C13		2.86	4.72
C14		2.88	5.74
C15		1.01	3.39
C16	1.32		2.58
C17	0.93		2.07
C18	0.96		2.18
E5	1.34*		2.60
E13		3.21	4.76
E14		2.65	4.09
E15		0.95	1.55
E16	2.05		3.21
E17	0.66		2.36
E18	1.04		2.57

*Sum of $Y_{Ca} + Y_{Na}$.

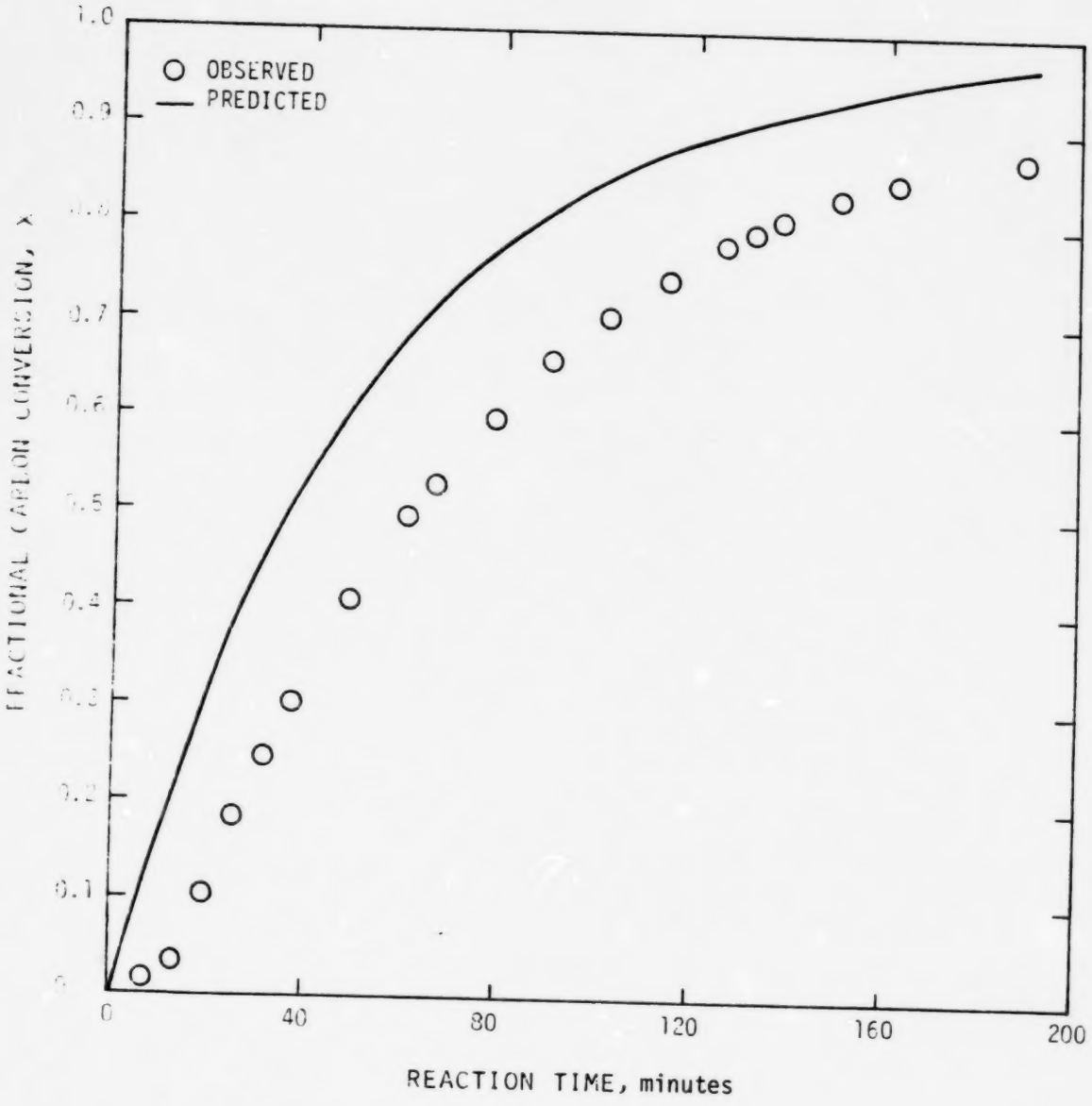

Figure 8. COMPARISON OF OBSERVED AND PREDICTED ROM CARBON CONVERSION FOR THE STEAM GASIFICATION OF C5 CHAR (PREDICTION BASED ON k' CALCULATED FROM EQUATION (5)

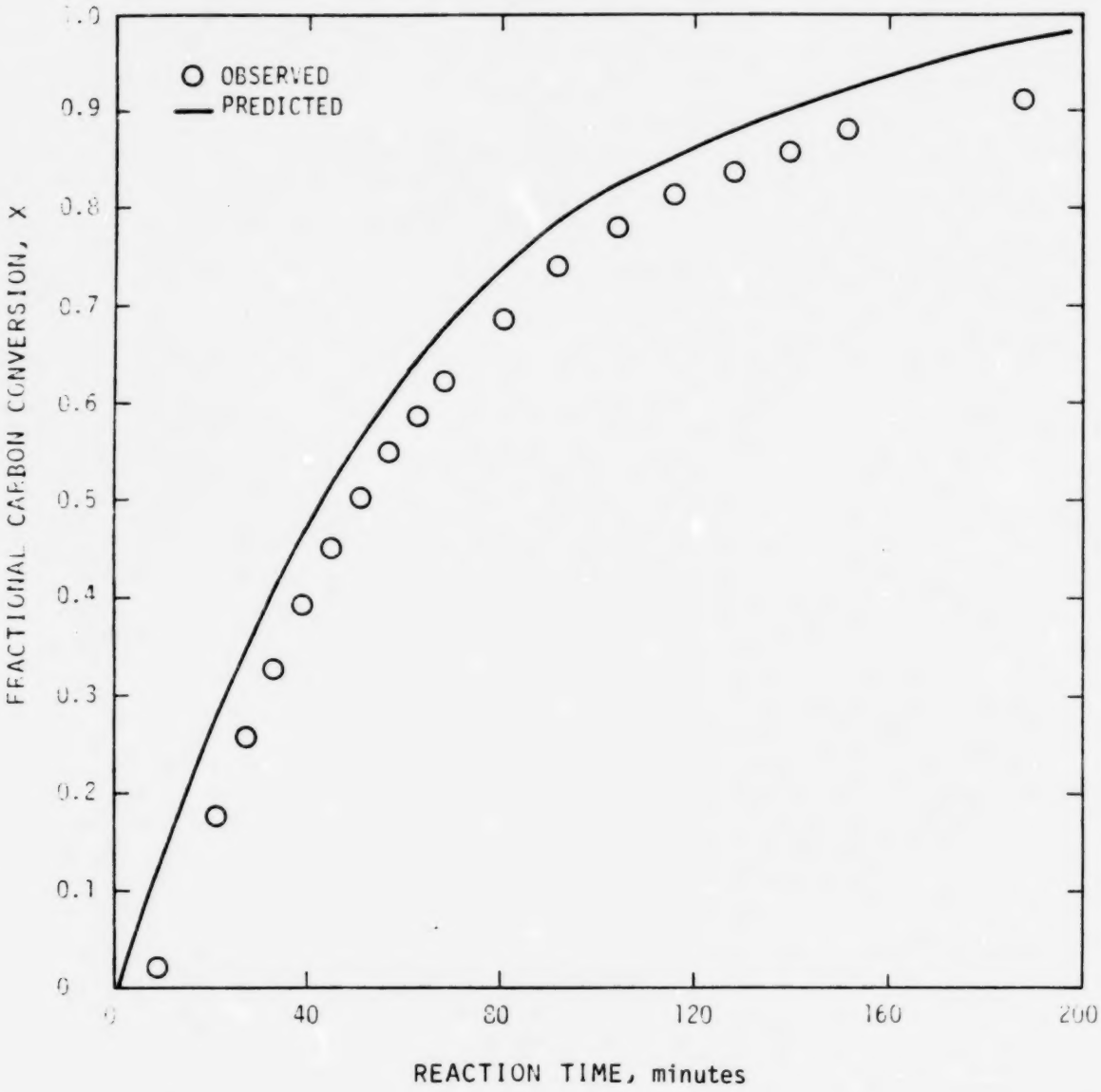

Figure 9. COMPARISON OF OBSERVED AND PREDICTED ROM CARBON CONVERSION FOR THE STEAM GASIFICATION OF E5 CHAR (PREDICTION BASED ON k' CALCULATED FROM EQUATION (5))

greater than actual experimental data. This difference can be explained in the following ways:

1) There is an inductive time period in steam gasification runs, during which the gasification rate is low (Figure 6); and,

2) Equation (5) correlates the catalytic effect of sodium and calcium in the form of salts of acidic functional groups; however, the contents of these metals reported in the analysis of ROM lignites (Table 7), include sodium and calcium present in other forms in ROM coals. Therefore, the k' values have been overestimated when used to predict the gasification characteristics of ROM lignite. To overcome this discrepancy, only concentrations of ion-exchangeable sodium and calcium should be used to calculate k' values. Although, the exchangeable cation content of ROM lignites can be determined by proton exchange with acetic or other weak acids, these values were not determined in this work.

Despite the difference of 5 to 20 percent between experimental and predicted carbon conversion, equation (5) provides a good approximation of lignite gasification behaviour. Most importantly, it permits quantification of the effect of variation of lignite composition on lignite gasification reactivity.

The second method of theoretical treatment of gasification kinetics was based on the method developed by Mahajan et al. (1978) in which carbon conversion data is plotted vs. dimensionless time, (τ) which is

defined by equation (6):

$$\tau = \frac{\text{time}}{t_{1/2}} \qquad (6)$$

where $t_{1/2}$ is the time required to gasify half of the initial carbon in the char.

Mahajan et al. (1978) observed that one s-shaped curve can be obtained for coals gasified at different temperatures and pressures when conversion data were plotted vs. the dimensionless parameter, t. The practical significance of the s-shaped curve is obvious, since gasification reactivity and carbon conversion, can be described by one parameter, $t_{1/2}$. Thus, analysis of gasification reactivity would require determination of $t_{1/2}$ alone, making detailed evaluation of carbon conversion vs. time relationships unnecessary. Figures 10 through 13 present these plots for Estevan and Coronach, ROM and treated coals. Essentially identical plots were obtained for all steam gasification runs. As predicted these plots are s-shaped with an inductive period, at early stages of gasification. Table 8 presents $t_{1/2}$ values for ROM, acid-washed and treated lignites.

For comparison purposes, half time values have been calculated from the experimental rate constants, k' using equation (7) and are presented as $t'_{1/2}$ in Table 8:

$$t'_{1/2} = \frac{\ln(2)}{k'} \qquad (7)$$

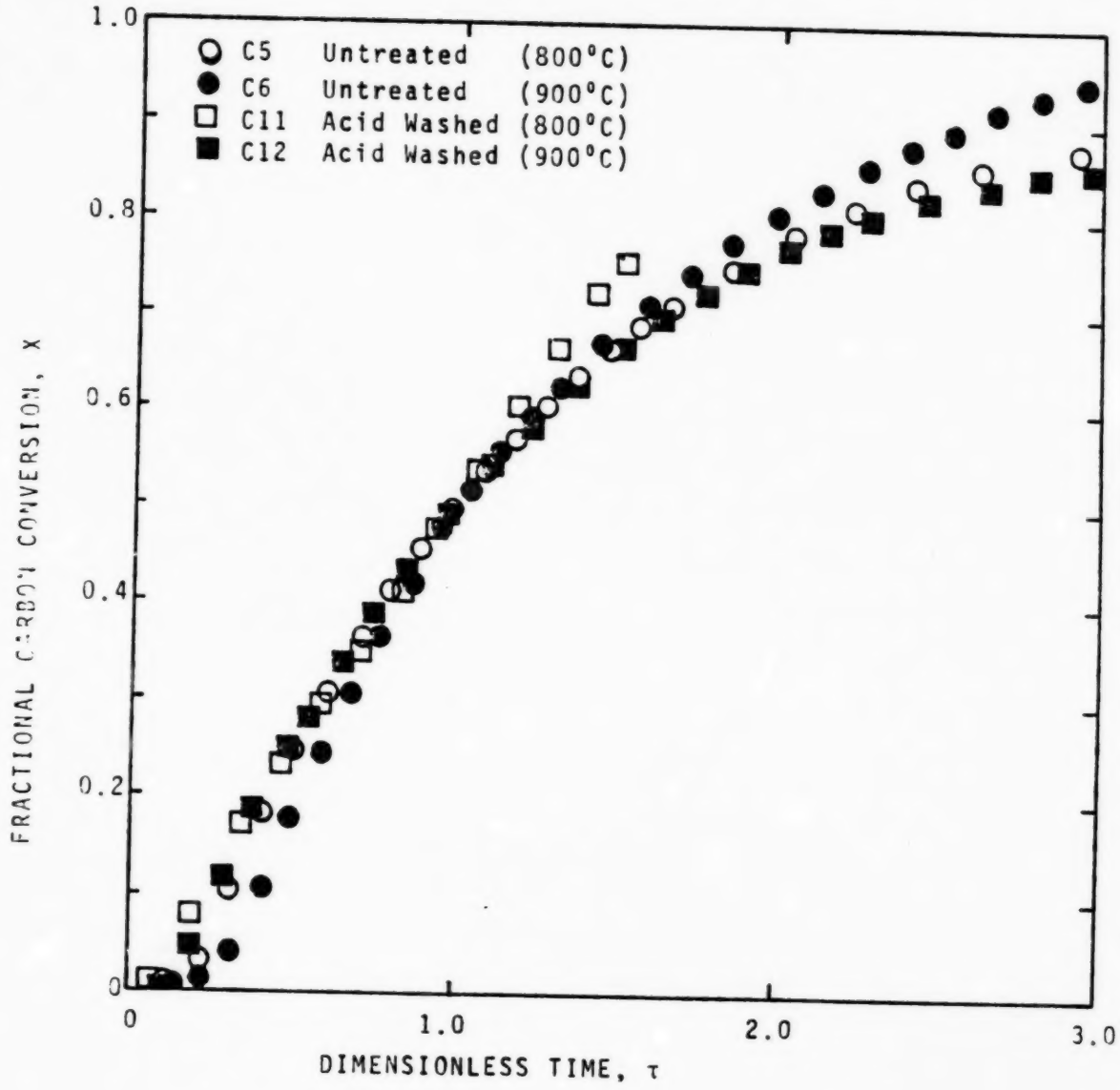

Figure 10. FRACTIONAL CARBON CONVERSION VS. DIMENSIONLESS TIME FOR THE STEAM GASIFICATION OF CORONACH CHARS AT 2 MPa

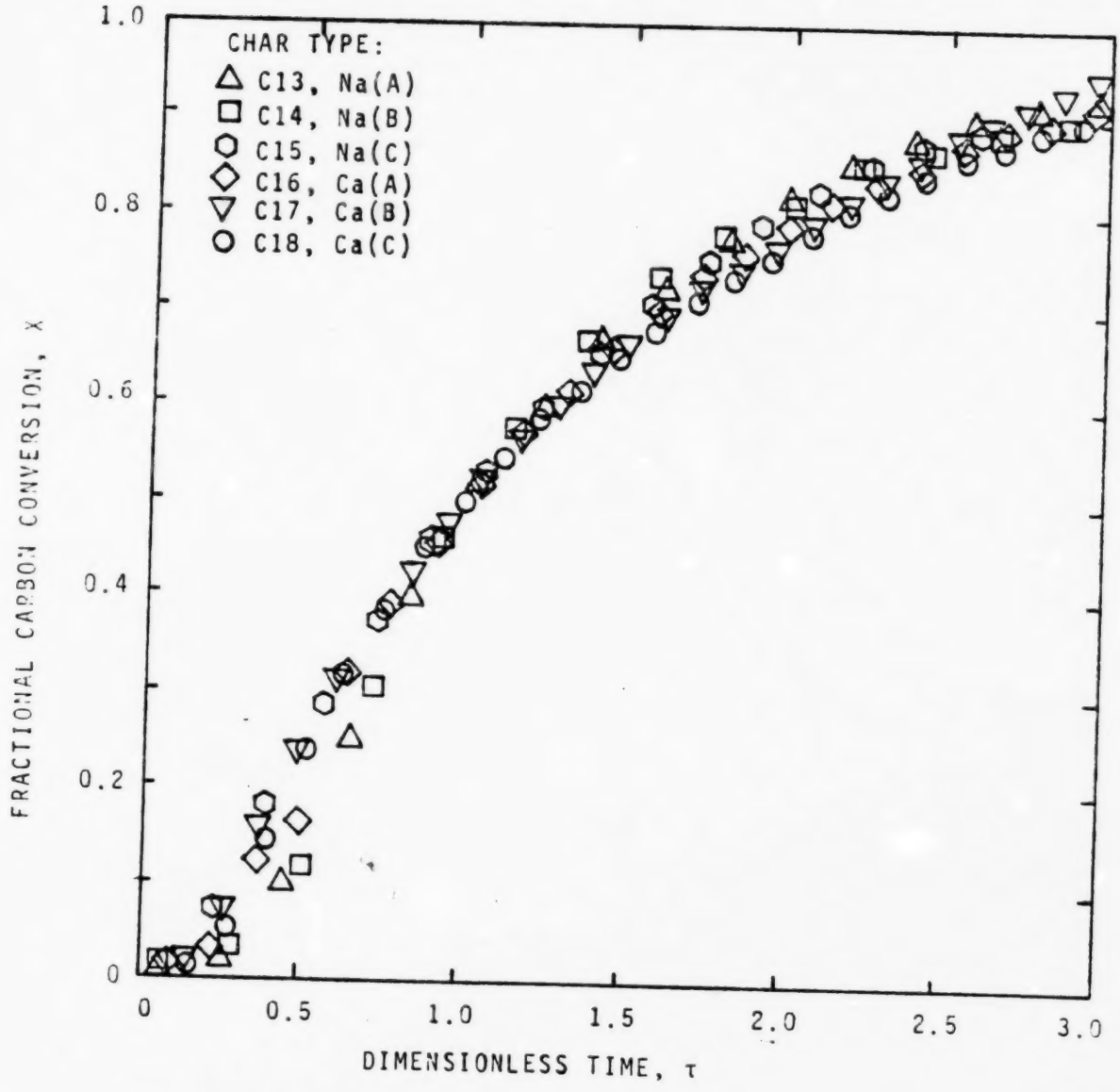

Figure 11. FRACTIONAL CARBON CONVERSION VS. DIMENSIONLESS TIME FOR THE STEAM GASIFICATION OF CORONACH CHARS AT 2 MPa

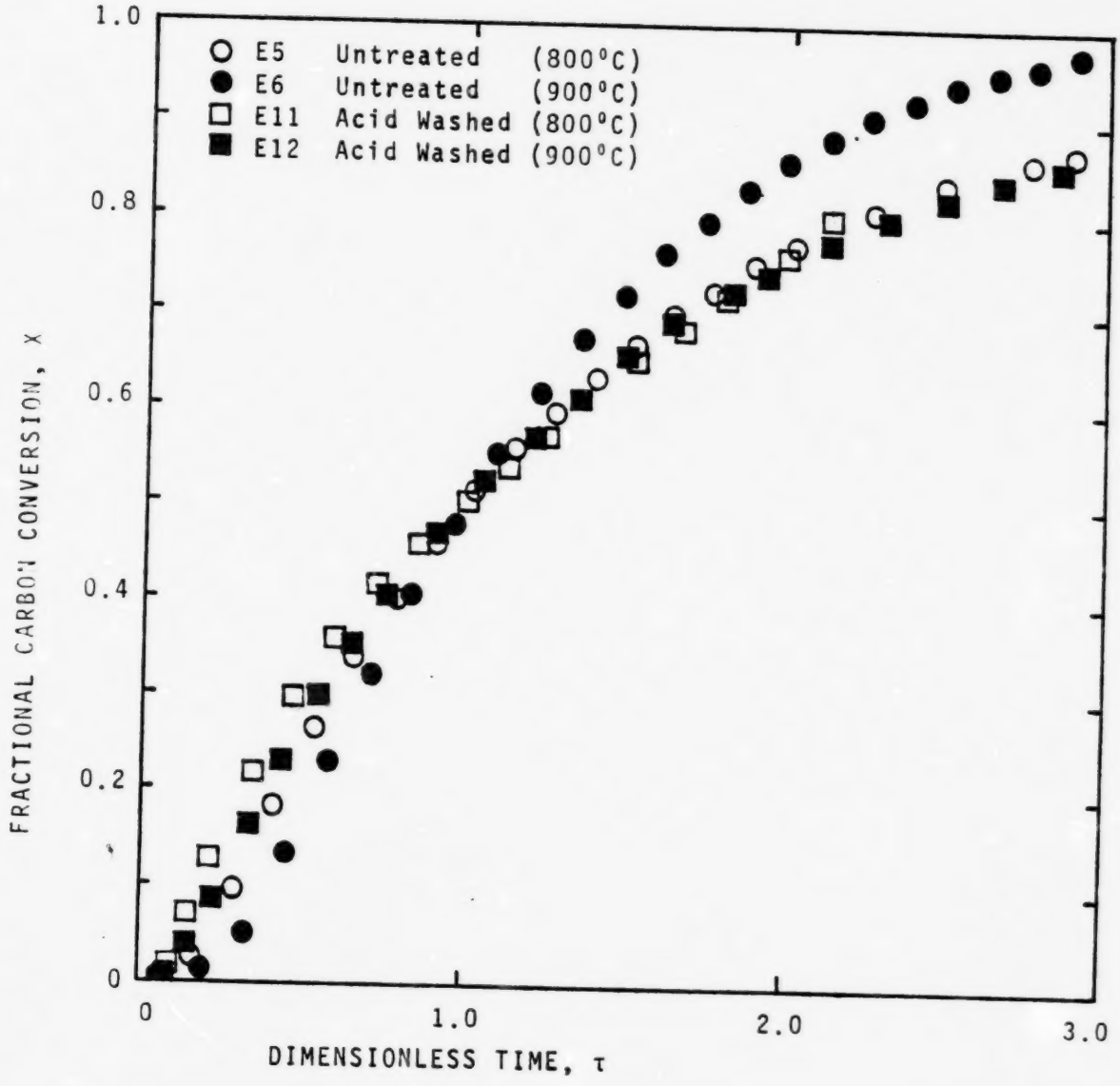

Figure 12. FRACTIONAL CARBON CONVERSION VS. DIMENSIONLESS TIME FOR THE STEAM GASIFICATION OF ESTEVAN CHARS AT 2 MPa

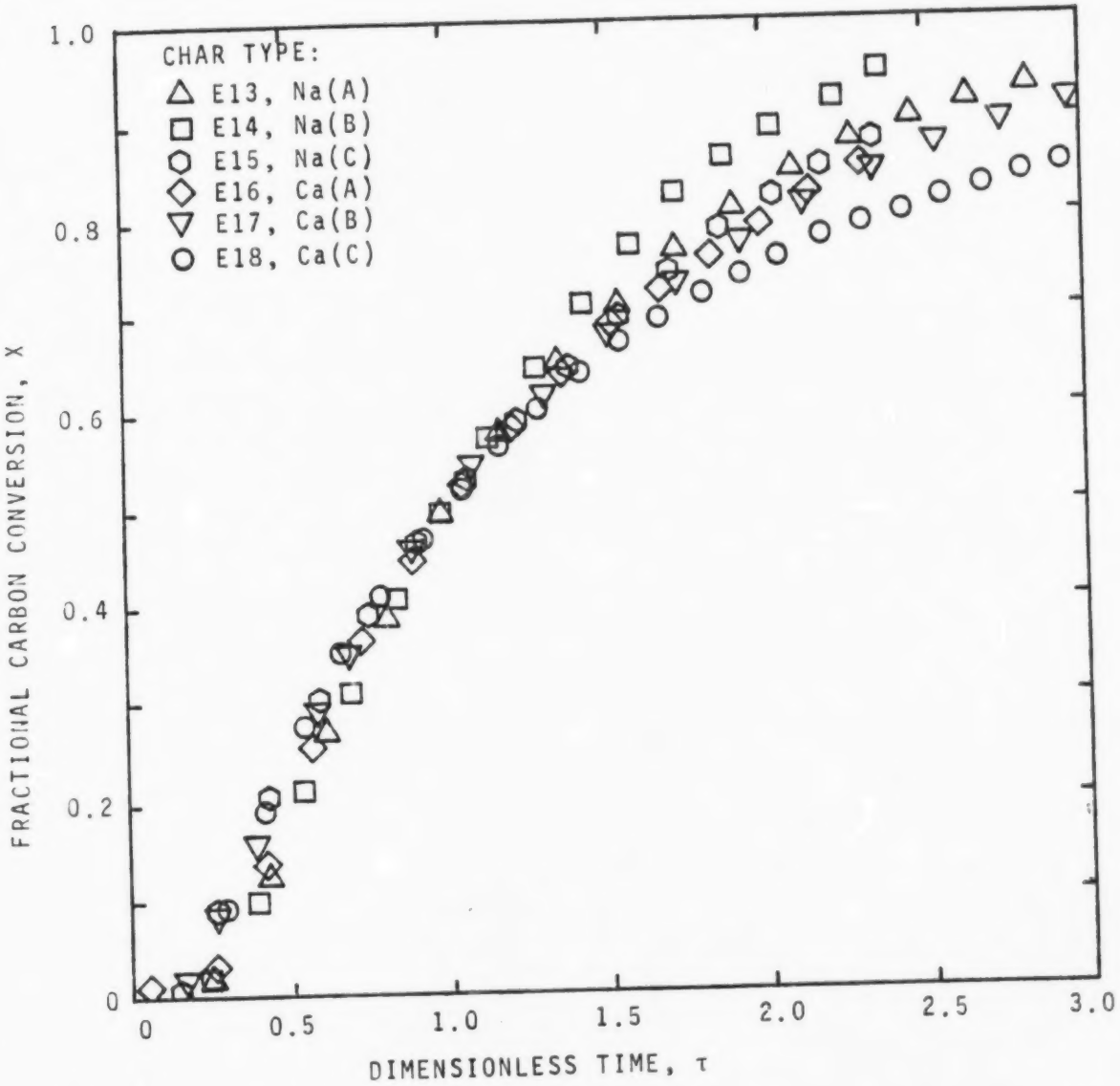

Figure 13. FRACTIONAL CARBON CONVERSION VS. DIMENSIONLESS TIME FOR THE STEAM GASIFICATION OF ESTEVAN CHARS AT 2 MPa

Table 8. COMPARISON OF OBSERVED AND CALCULATED HALF-TIMES FOR LIGNITE CHARS GASIFIED IN STEAM AT 2 MPa

Sample	Type	Temperature (°C)	$t_{1/2}$ (minutes)	$t'_{1/2}$ (minutes)
		Coronach		
C5	ROM	800	62.5	52.3
C6	ROM	900	44.1	34.9
C11	A-W	800	150.0	94.7
C12	A-W	900	61.3	54.2
C13	Na(A)	800	31.1	20.1
C14	Na(B)	800	27.8	16.5
C15	Na(C)	800	35.5	27.9
C16	Ca(A)	800	45.3	36.7
C17	Ca(B)	800	53.1	45.7
C18	Ca(C)	800	58.2	43.5
		Estevan		
E5	ROM	800	48.5	41.4
E6	ROM	900	31.0	19.1
E11	A-W	800	94.1	107.6
E12	A-W	900	54.7	57.2
E13	Na(A)	800	32.4	22.6
E14	Na(B)	800	41.9	26.3
E15	Na(C)	800	76.6	69.3
E16	Ca(A)	800	40.7	33.6
E17	Ca(B)	800	57.9	45.6
E18	Ca(C)	800	47.6	44.2

The difference between $t_{1/2}$ and $t'_{1/2}$ is due to the inductive period observed in steam gasification runs (Figures 10-13).

The correlation between $t_{1/2}$ values and enriched lignite composition is presented graphically in Figure 14. The correlation coefficients are: $R^2 = .522$ and $\alpha = 2.84$ for the equation:

$$t_{1/2} = 62.7 - 10.36(Y) \times 10^3 \qquad (8)$$

where Y = concentration of Na^+ and/or Ca^{++} in moles/g F.C.

Due to these poor statistical coefficient (i.e., $R^2 = 0.52$ and $\alpha = 2.84$) prediction of $t_{1/2}$ based on lignite cation composition should not provide a good approximation of ROM lignite char gasification behaviour. However, Figures 15 and 16 show that the correlation with actual ROM gasification data is much better than when predicted using the correlation for the apparent rate constant k' (equation 5). The accuracy of these predictions is due to the fact that the data for both ROM lignites falls very close to the least squares' line. If other ROM coals had been tested, the low R^2 value suggests that less accurate predictions would result.

It is concluded therefore that the dimensionless time parameter, τ, based on the experimental determination of $t_{1/2}$, provides good correlation to experimental carbon conversion data (Figures 17 and 18). However, when this approach is extended to correlate gasification reactivity with lignite composition, the approximation will be questionable. This is demonstrated in Figures 19 and 20, where equation (8) (i.e., $t_{1/2} = 62.7\text{-}10.36(Y) \times 10^3$;

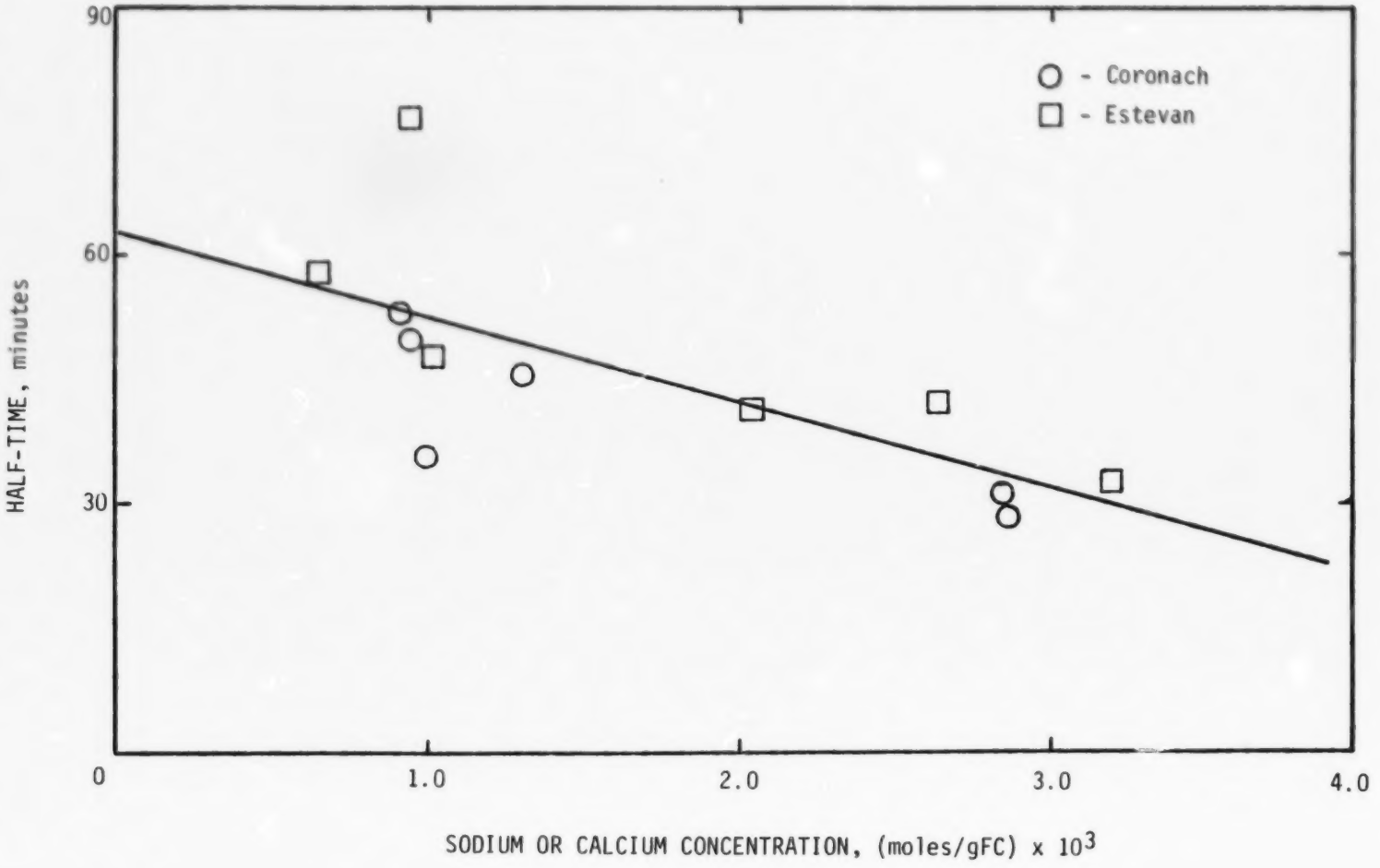

Figure 14. EFFECT OF SODIUM OR CALCIUM CONCENTRATION ON THE STEAM GASIFICATION HALF-TIME OF CATION ENRICHED LIGNITE CHARS AT 800°C AND 2 MPa

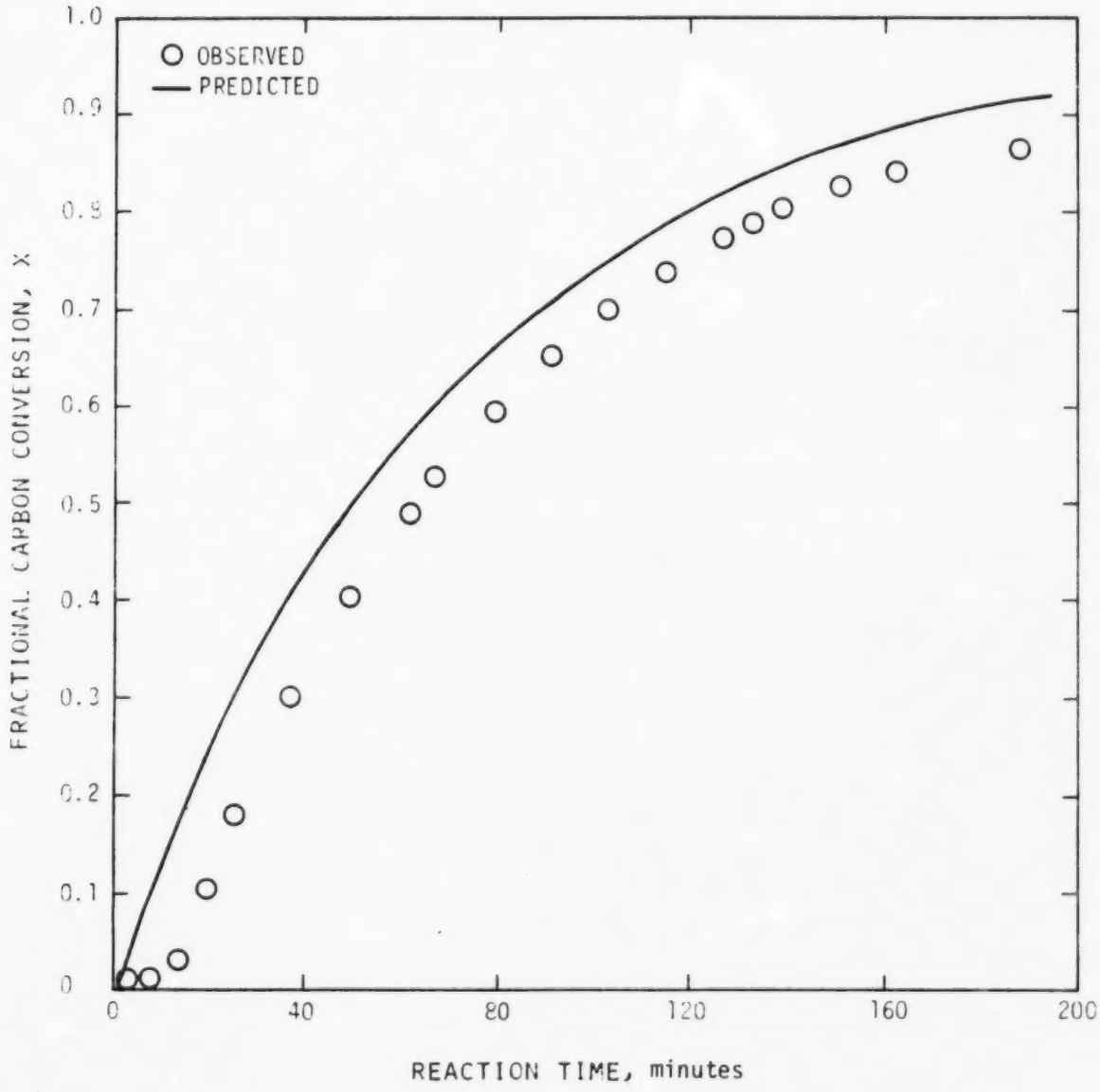

Figure 15. COMPARISON OF PREDICTED AND OBSERVED ROM CARBON CONVERSION FOR THE STEAM GASIFICATION OF C5 CHAR (PREDICTION BASED ON $t_{1/2}$ CALCULATED FROM EQUATION (8))

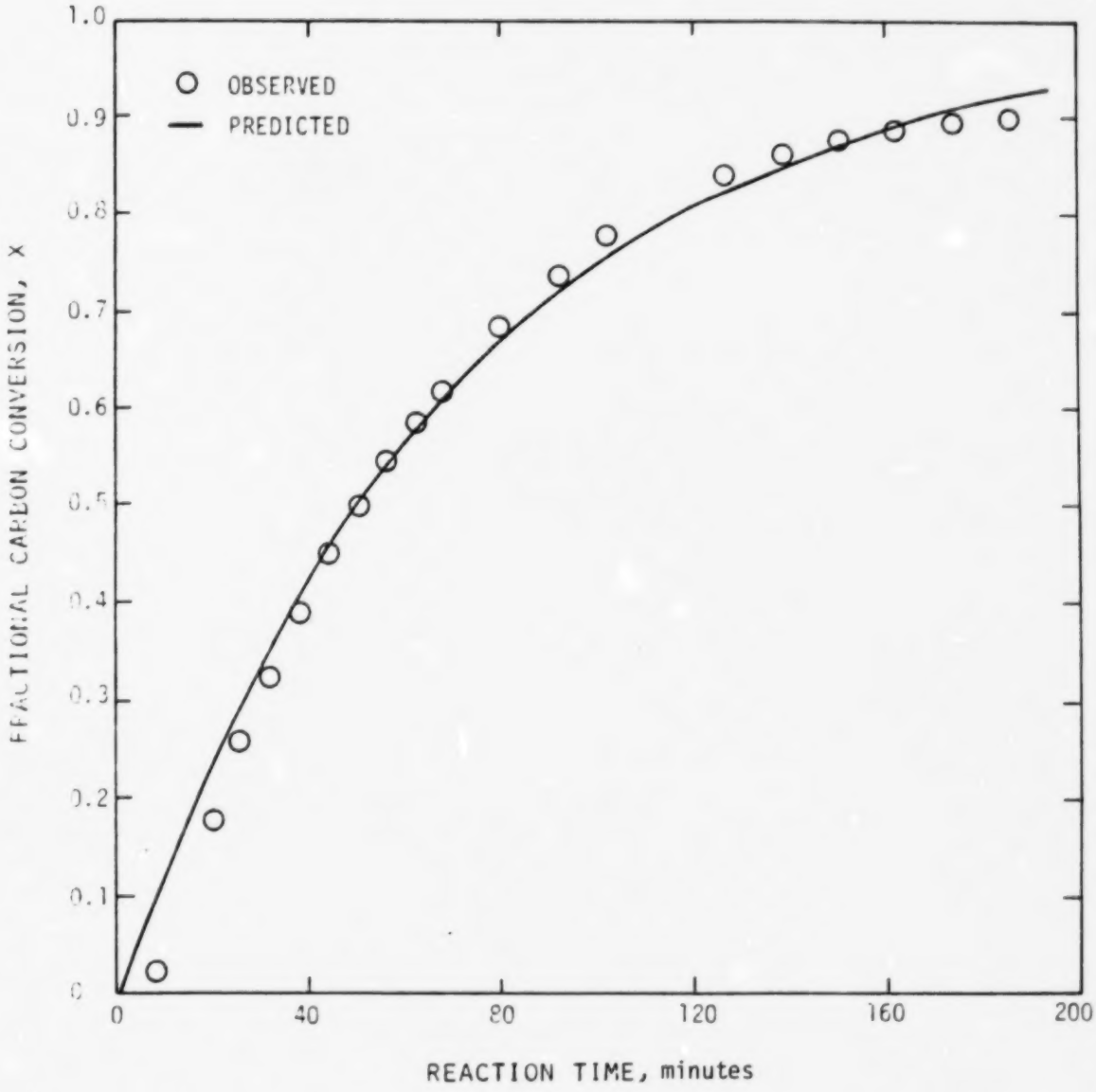

Figure 16. COMPARISON OF PREDICTED AND OBSERVED ROM CARBON CONVERSION FOR THE STEAM GASIFICATION OF E5 CHAR (PREDICTION BASED ON $t_{1/2}$ CALCULATED FROM EQUATION (8))

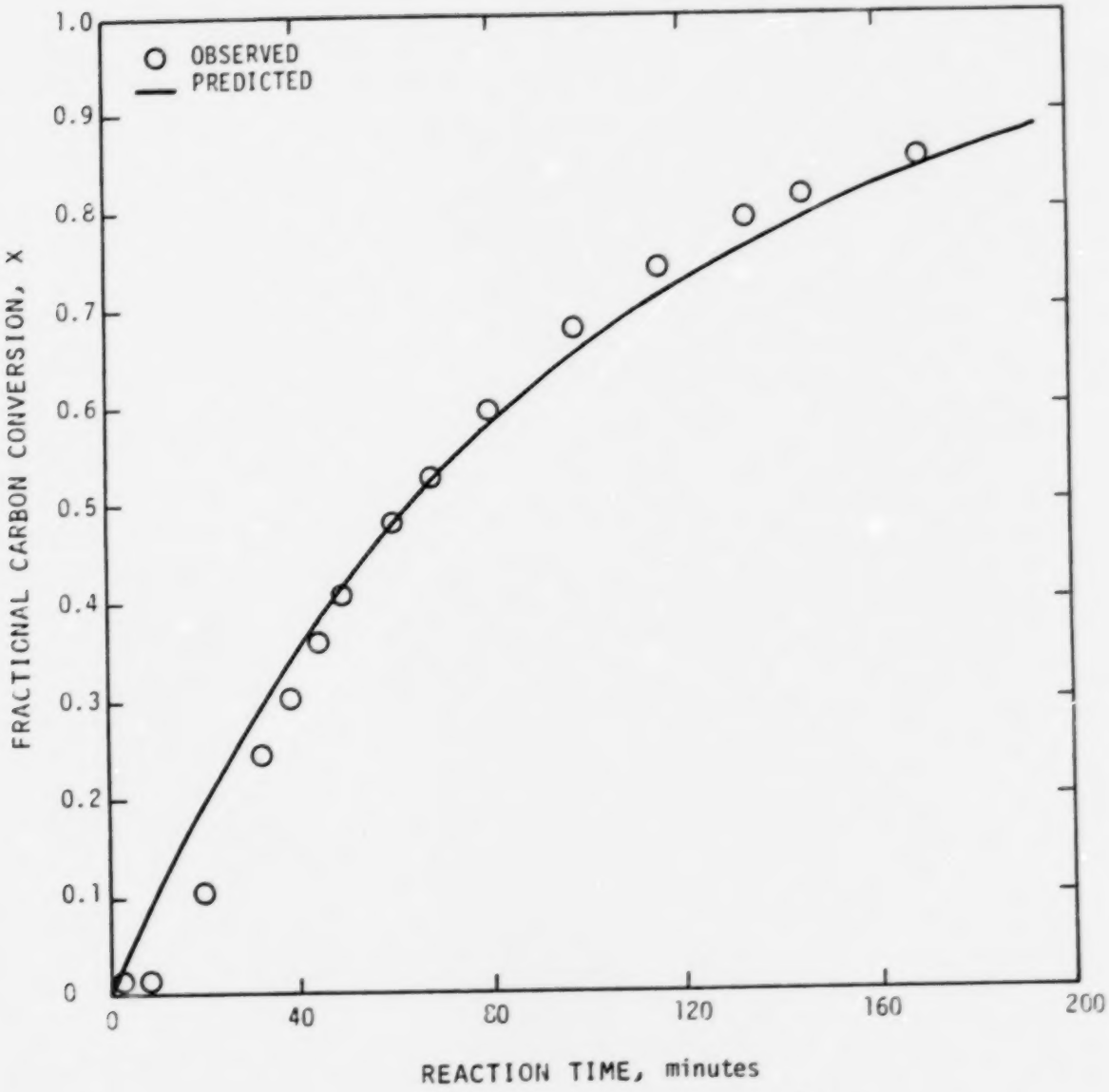

Figure 17. COMPARISON OF PREDICTED AND OBSERVED ROM CARBON CONVERSION FOR THE STEAM GASIFICATION OF C5 CHAR (PREDICTION BASED ON k' CALCULATED FROM $t_{1/2}$)

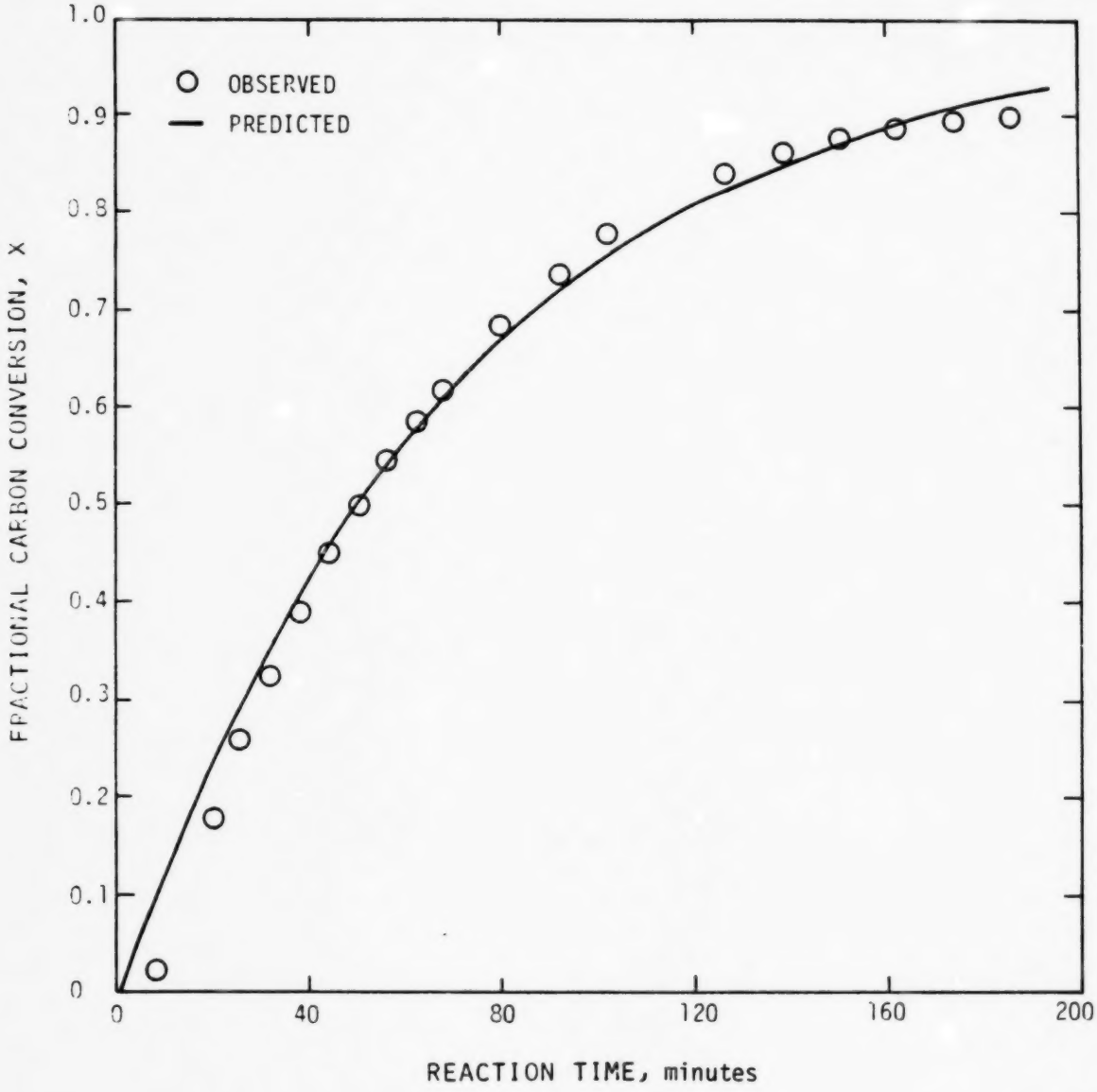

Figure 18. COMPARISON OF PREDICTED AND OBSERVED ROM CARBON CONVERSION FOR THE STEAM GASIFICATION OF E5 CHAR (PREDICTION BASED ON k' CALCULATED FROM $t_{1/2}$)

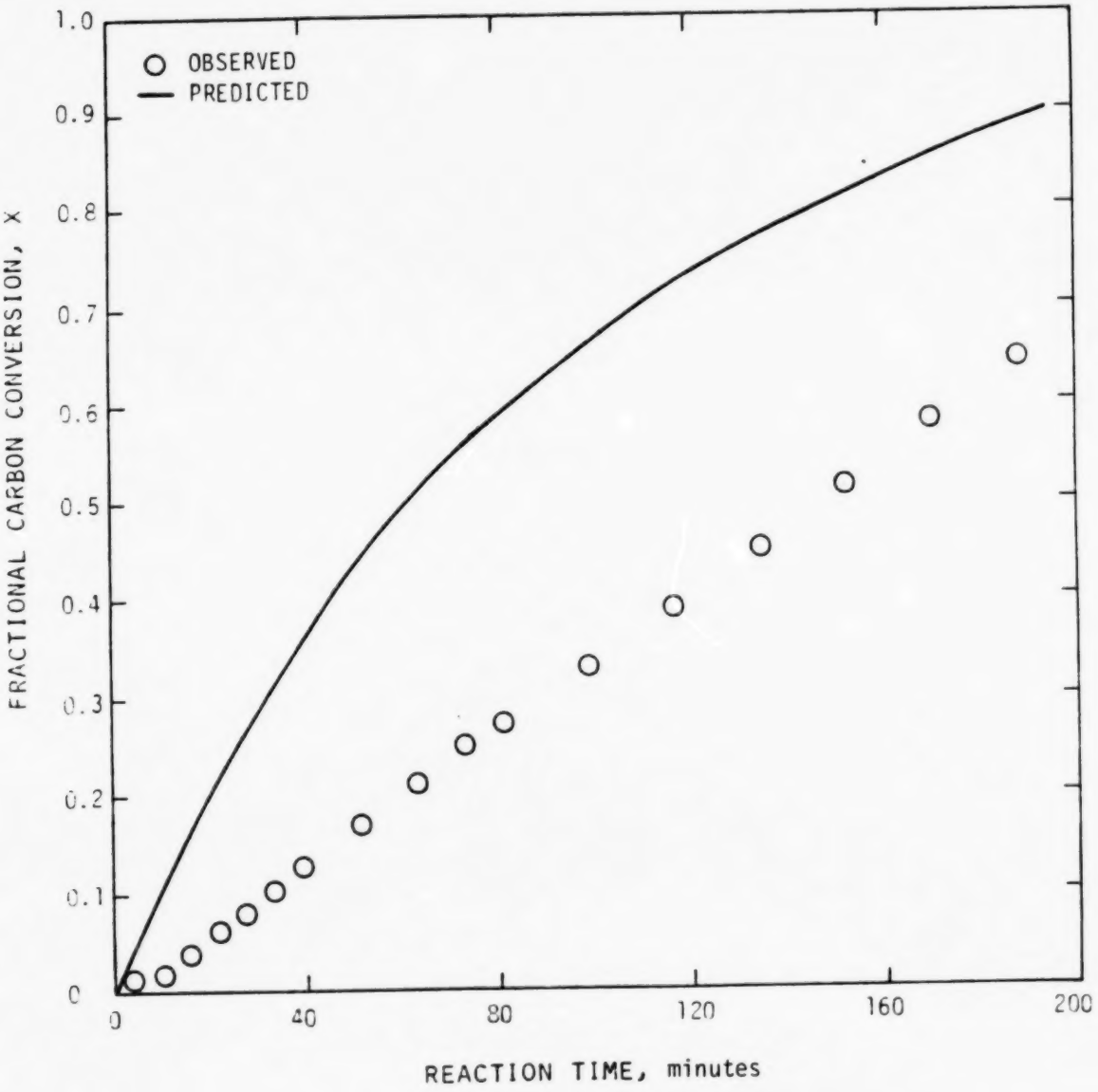

Figure 19. COMPARISON OF PREDICTED AND OBSERVED ACID-WASHED CARBON CONVERSION FOR THE STEAM GASIFICATION OF C11 CHAR (PREDICTION BASED ON $t_{1/2}$ CALCULATED FROM EQUATION (8))

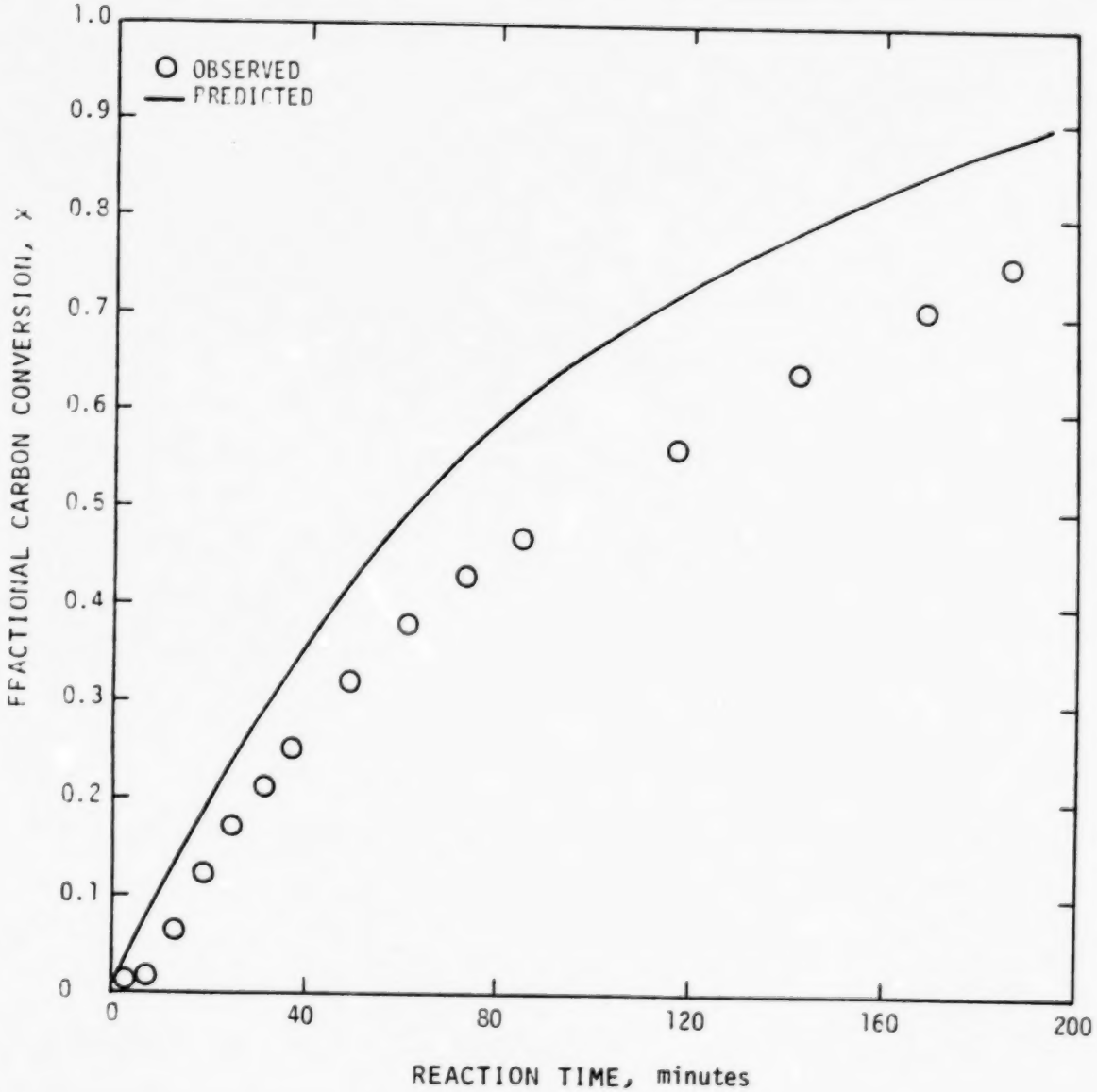

Figure 20. COMPARISON OF PREDICTED AND OBSERVED ACID-WASHED CARBON CONVERSION FOR THE STEAM GASIFICATION OF E11 CHAR (PREDICTION BASED ON $t_{1/2}$ CALCULATED FROM EQUATION (8))

for Y = 0; $t_{1/2}$ = 62.7) is used to predict acid-washed char reactivity. The inductive period due to changes in char surface area and porosity at the early stages of gasification precludes consistently accurate prediction of $t_{1/2}$ from lignite composition.

Air/Steam Gasification of Chars Derived from Untreated and Acid-Washed Coals

The analysis of steam/air gasification kinetics involved the same two theoretical methods as used for steam gasification runs. Observation of carbon conversion data (Figure 21) showed that steam/air char gasification proceeds according to zero order kinetics. The zero order rate expression (9):

$$\text{Rate} = k''' \tag{9}$$

upon integration yields (10):

$$I(X) = X = k'''t \tag{10}$$

which provides a method for direct calculation of the apparent rate constant k''' from the slope of the fractional carbon conversion vs. time graph (Figure 21).

The integrated rate expression (10) gave a good fit to experimental data over the range of carbon conversion X = 0.1 to 0.9. Values for the apparent rate constant k''' are presented in Table 9 for both ROM and

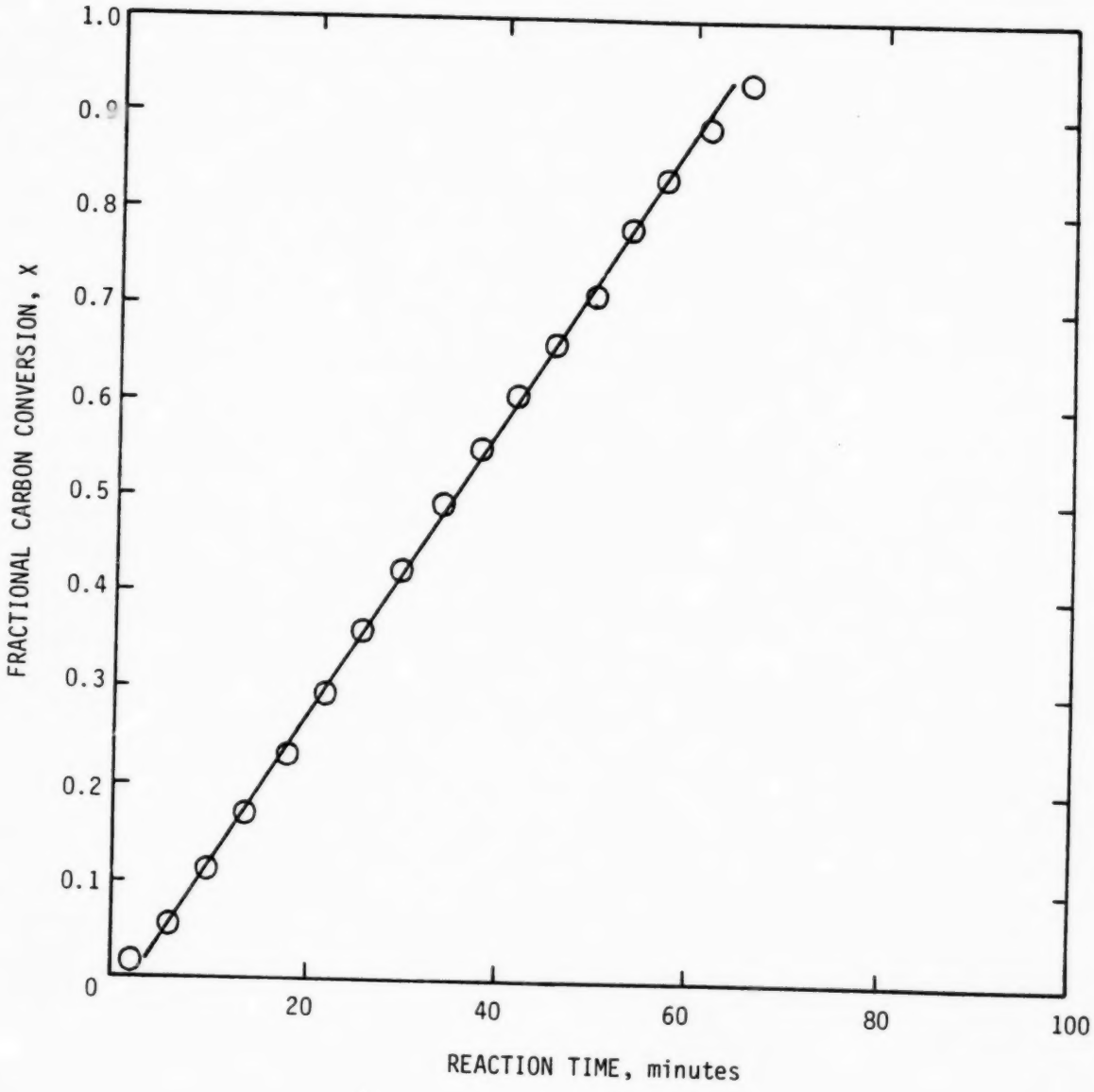

Figure 21. ZERO ORDER KINETICS FOR THE STEAM/AIR GASIFICATION OF ROM CHAR AT 900°C AND 2 MPa

Table 9. KINETIC PARAMETERS FOR THE STEAM/AIR GASIFICATION OF ROM AND ACID-WASHED CHARS

Sample	Type	Temperature (°C)	Pressure (MPa)	k' X 102 (min-1)	Reactivity Ratio k'/k'o
			Coronach		
C1	ROM	800	0.1	1.538	2.167
C2	ROM	900	0.1	1.975	1.778
C3	ROM	800	2.0	1.500	0.907
C4	ROM	900	2.0	1.633	0.988
C7	A-W	800	0.1	0.710	
C8	A-W	900	0.1	1.111	
C9	A-W	800	2.0	1.653	
C10	A-W	900	2.0	2.049	
			Estevan		
E1	ROM	800	0.1	1.528	1.852
E2	ROM	900	0.1	1.909	1.850
E3	ROM	800	2.0	1.434	1.092
E4	ROM	900	2.0	1.621	0.904
E7	A-W	800	0.1	0.825	
E8	A-W	900	0.1	1.032	
E9	A-W	800	2.0	1.313	
E10	A-W	900	2.0	1.794	

acid-washed lignite chars.

Similar to the approach used for steam gasification analysis, the reactivity ratios k'''/k'''_o were tested for correlation with lignite composition. No clear relationship was indicated by this plot. However, the reactivity ratio data presented in Table 9 follows certain trends. For steam/air gasification runs conducted at 2 MPa pressure the reactivity ratios, k'''/k'''_o, are about 1 or in other words, independent of Na^+ or Ca^{++} concentrations in lignite. Reactivity ratios for atmospheric pressure (i.e., 0.1 MPa) steam/air gasification range from 1.7 to 2.2 indicating an apparent catalytic effect due to the exchangeable Na^+ or Ca^{++} concentrations in the lignite. Several plausible explanations can be proposed for this observation such as a change of the rate controlling step. The most likely cause for these observations will be elaborated in the next phase of this program.

The second method used for the analysis of steam gasification kinetics was based on the dimensionless time parameter, τ. The zero order rate expression when expressed in terms of the time for conversion of half of the initial carbon in the char becomes (11):

$$I(X) = 0.5 = k'''t_{1/2} \qquad (11$$

Thus, knowing the one parameter, $t_{1/2}$, the apparent rate constant can be estimated. Figures 22 and 23 show the very good agreement between the carbon conversion predicted on the basis of k''' calculated from equation (11) and actual gasification data. The conclusion was the same as that for

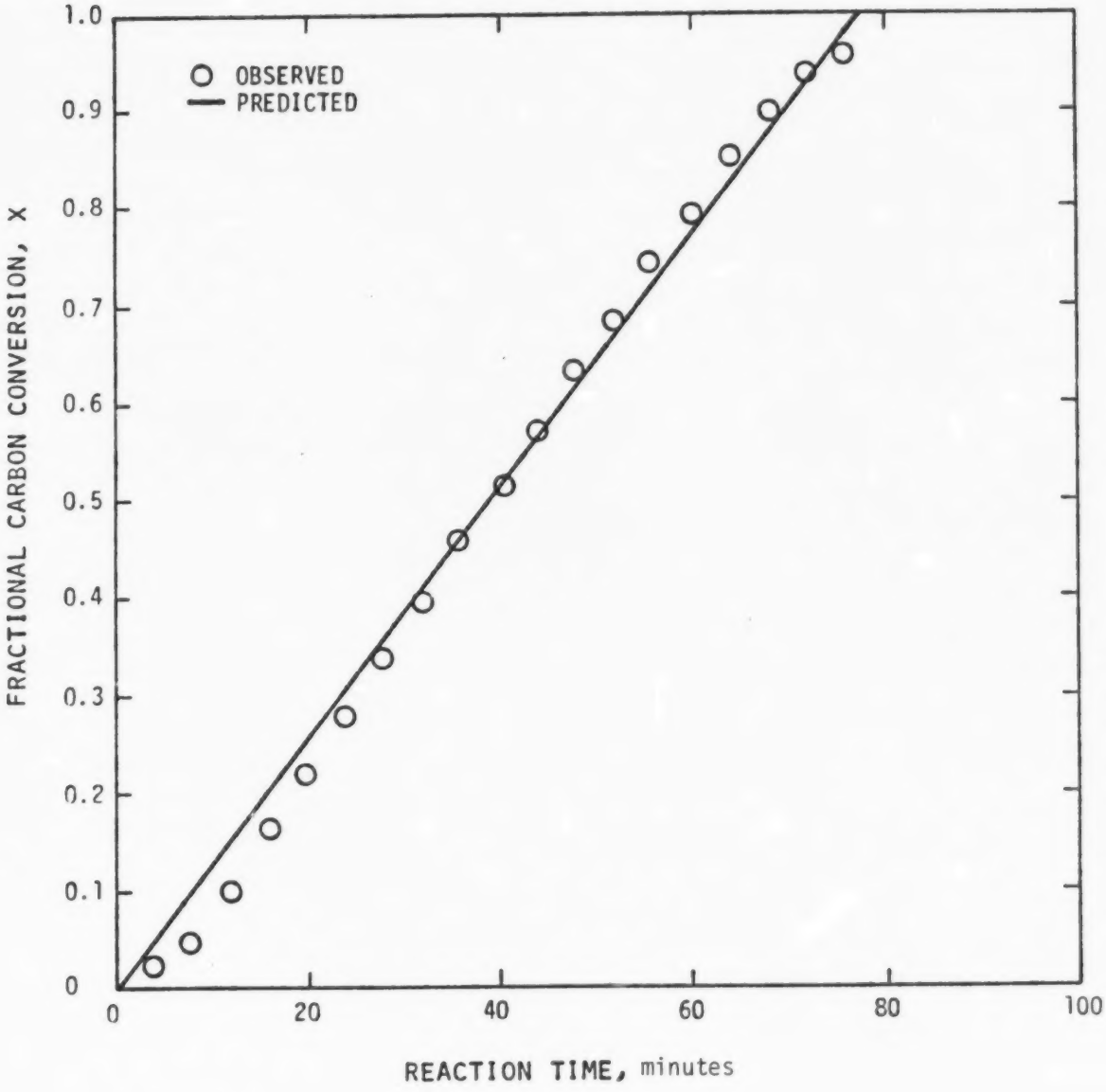

Figure 22. COMPARISON OF PREDICTED AND OBSERVED ROM CARBON CONVERSION FOR THE STEAM/AIR GASIFICATION OF C3 CHAR (PREDICTION BASED ON k''' CALCULATED FROM $t_{1/2}$)

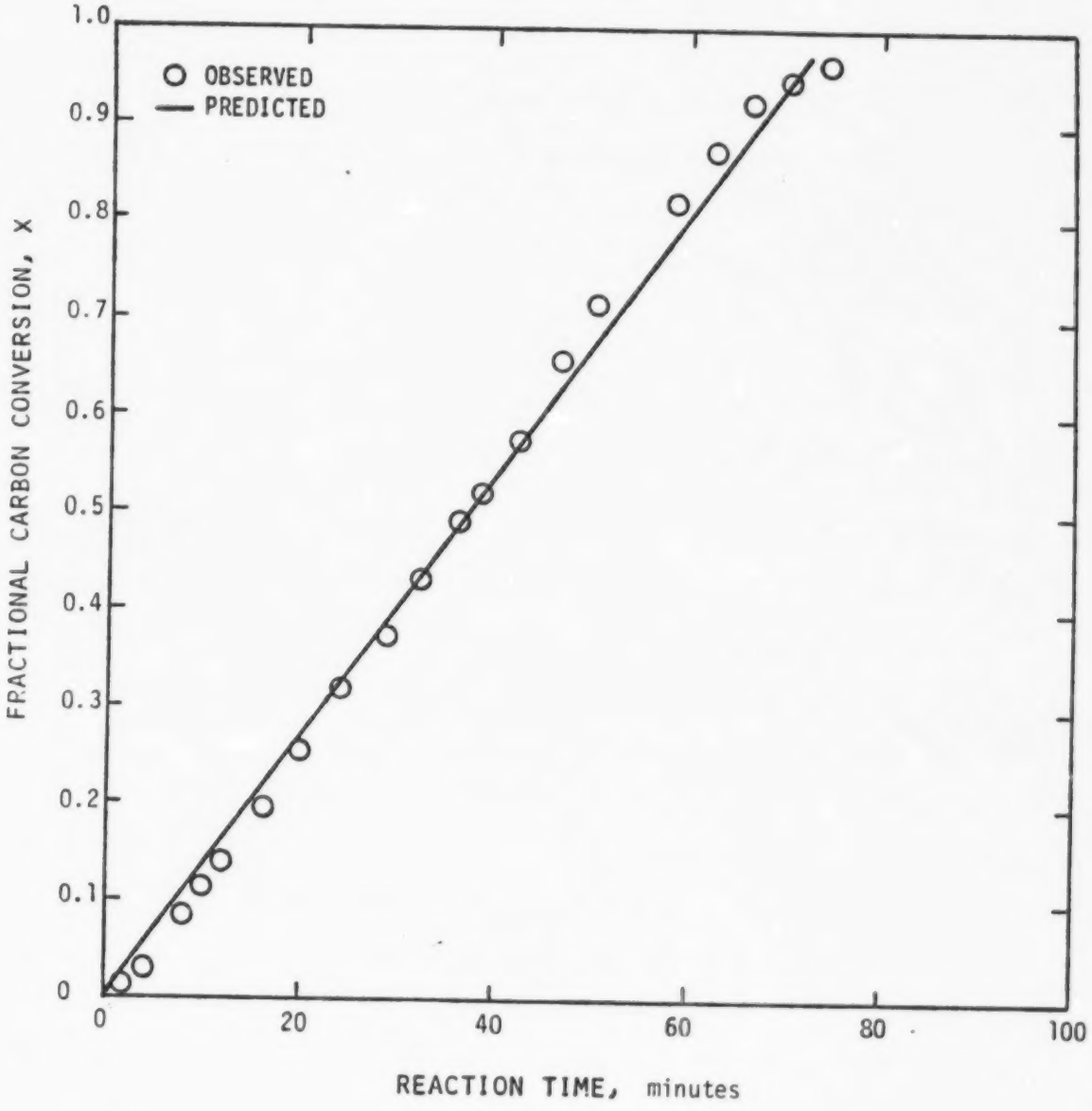

Figure 23. COMPARISON OF PREDICTED AND OBSERVED ROM CARBON CONVERSION FOR THE STEAM/AIR GASIFICATION OF E3 CHAR (PREDICTION BASED ON k''' CALCULATED FROM $t_{1/2}$)

the steam gasification of lignite chars. Analysis of air/steam char gasification reactivity would require the experimental determination of only one parameter, $t_{1/2}$.

Observation of steam/air gasification data indicated that the carbon-steam reaction may behave independently of other gasification reactions. In order that this theory holds true the oxygen consuming reaction (12):

$$C + O_2 \rightleftharpoons CO_2 \qquad (12)$$

must proceed considerably faster than the steam consuming reaction (13):

$$C + H_2O \rightleftharpoons CO + H_2 \qquad (13)$$

otherwise steam/air gasification would not proceed according to zero order kinetics but rather at some fractional order between zero and one.

It is known that at the reactor temperatures used in this work reaction (12) will consume incoming oxygen almost instantaneously and for typical gasifier operation the rate of carbon conversion due to oxygen will be dependent only on the flowrate of air into the gasifier. The air input to the gasifier was kept constant for all air/steam gasification runs at 5.0 L/min at standard conditions of 101.3 kPa and 0°C. The consumption of carbon due to steam, however, depends on the kinetics of the reaction at the temperatures and pressures under consideration. The results presented graphically in Figure 24 show that the assumption is indeed correct and the

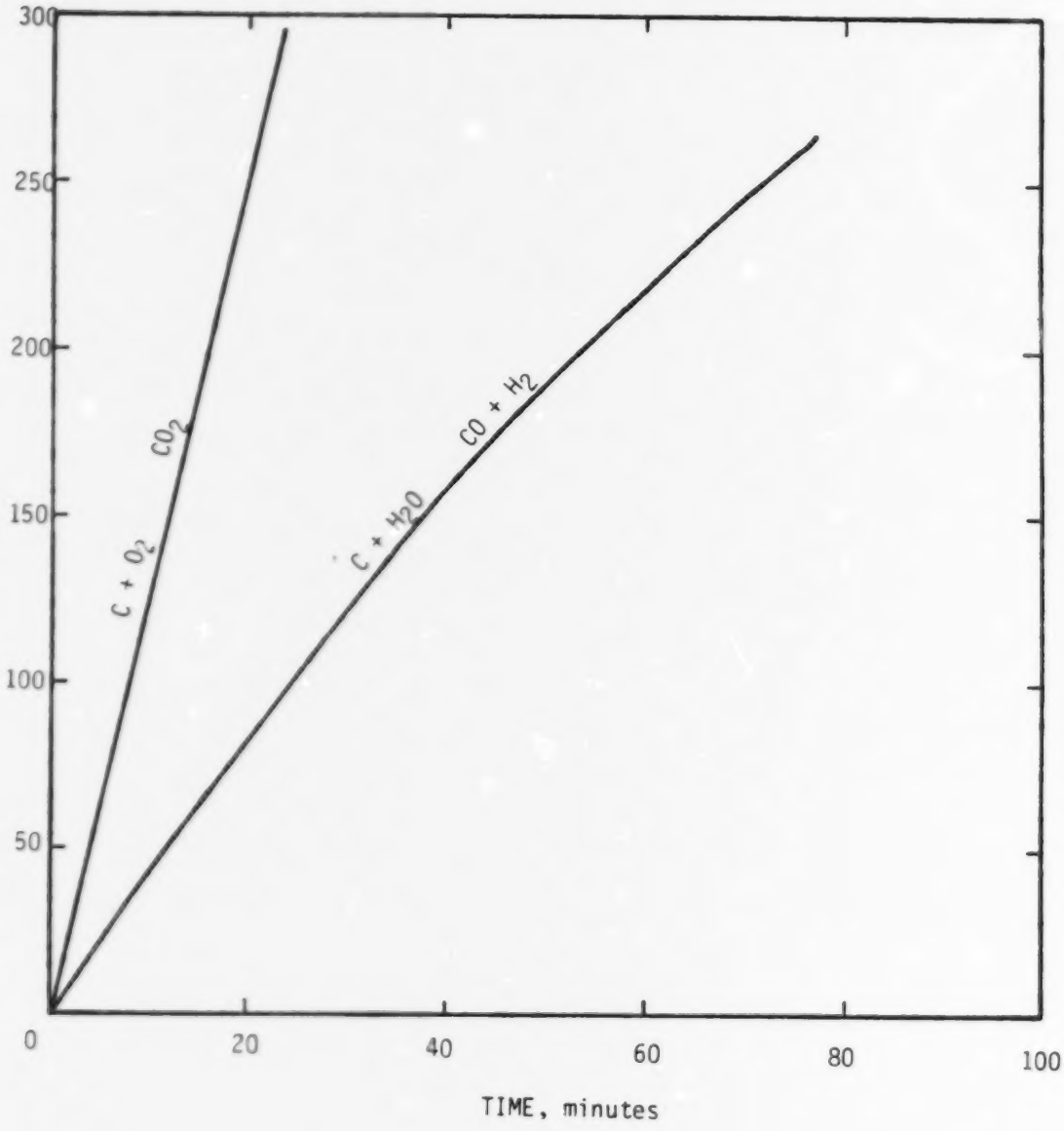

Figure 24. CUMULATIVE CARBON CONVERSION DUE TO STEAM AND OXYGEN

oxygen consuming reaction proceeds at about four times the rate of reaction (13). The fractional carbon conversion due to reactions (12) and (13) combined is compared with actual carbon conversion data in Figure 25. The extent of carbon conversion due to reactions (12) and (13) underestimates actual data by 24%.

The previous analysis, however, omitted the Boudard reaction (14):

$$C + CO_2 \rightleftharpoons 2CO \qquad (14)$$

which may account for this discrepancy. The double arrows in reaction (14) signify that the extent of carbon conversion will be dependent on equilibrium conditions inside the reactor. Assuming that the amount of CO_2 available in the reactor exit is at equilibrium with CO, a series of simultaneous equations can be solved in order that the amount of carbon removed by reaction (14) can be determined.
Detailed calculations and results are presented in Appendix A.

Figures 26 and 27 show the very good correlation between actual carbon conversion data and that predicted by the theoretical analysis of reactions (12), (13) and (14).

The results of this theoretical analysis demonstrates the usefulness of the dimensionless time parameter, τ. From one convenient measurement of

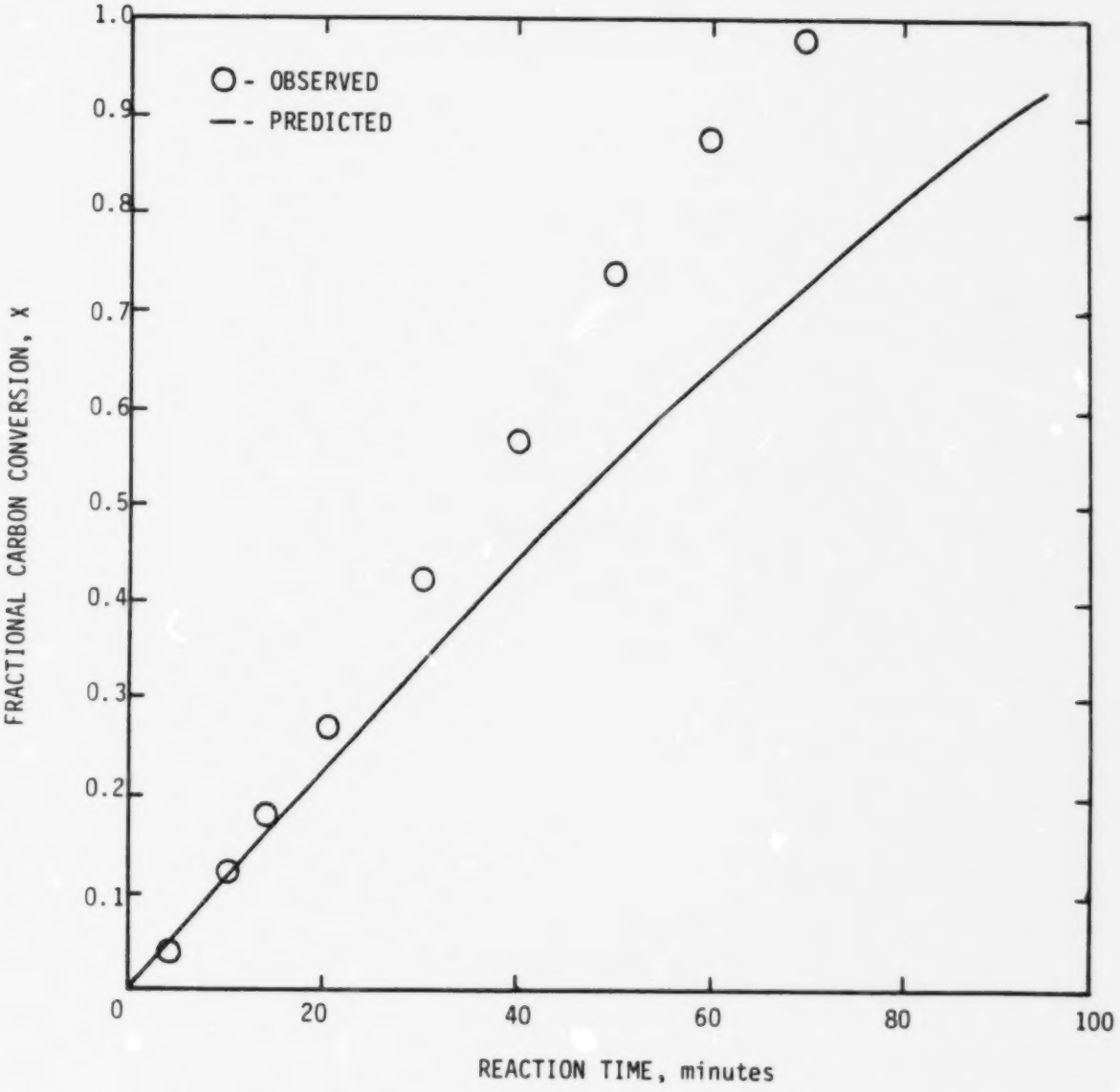

Figure 25. COMPARISON OF PREDICTED AND OBSERVED ROM CARBON CONVERSION FOR THE STEAM/AIR GASIFICATION OF E3 CHAR (PREDICTION BASED ON THE THEORETICAL TREATMENT OF REACTIONS OF (12) AND (13))

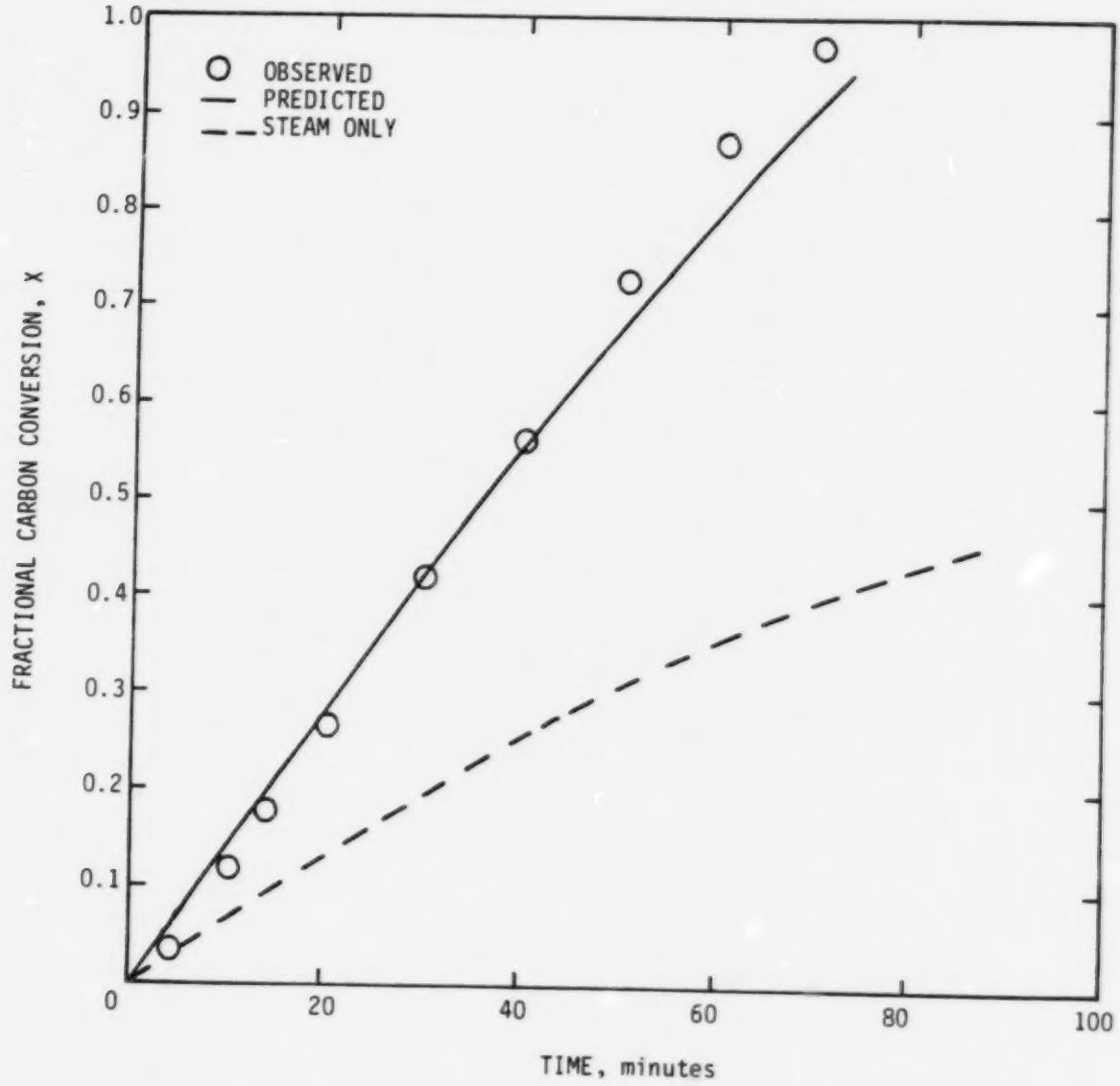

Figure 26. COMPARISON OF PREDICTED AND OBSERVED ROM CARBON CONVERSION FOR THE STEAM/AIR GASIFICATION OF E3 CHAR (PREDICTION BASED ON THEORETICAL TREATMENT OF REACTIONS (12), (13) AND (14))

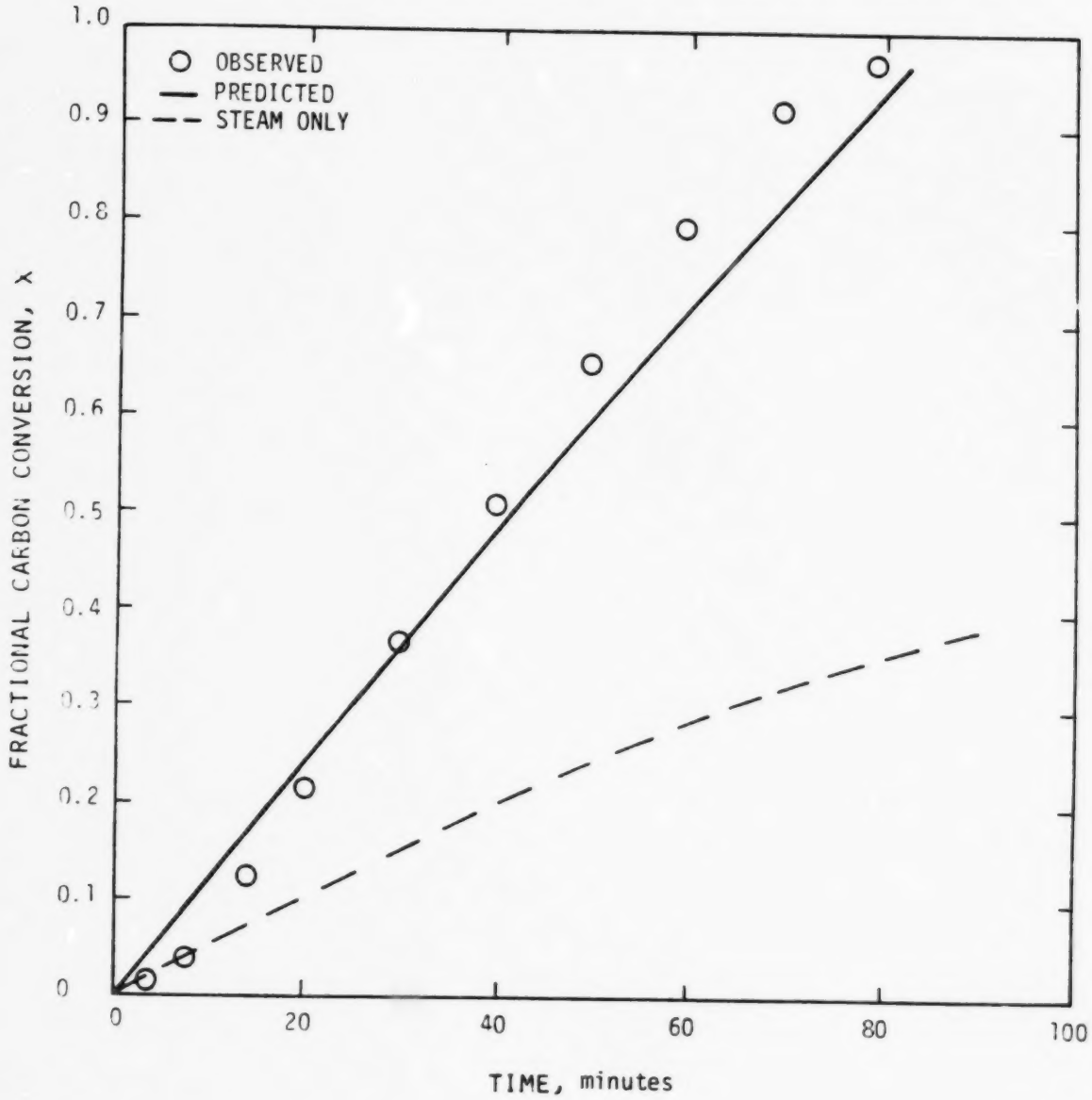

Figure 27. COMPARISON OF PREDICTED AND OBSERVED ROM CARBON CONVERSION FOR THE STEAM/AIR GASIFICATION OF C3 CHAR (PREDICTION BASED ON THEORETICAL TREATMENT OF REACTIONS (12), (13) AND (14))

$t_{1/2}$ for steam gasification, the result can be extrapolated to accurately predict steam/air char gasification behaviour.

CONCLUSIONS

The catalytic effect of Na^{+} and Ca^{++} on the gasification of Saskatchewan lignite chars in steam and steam/air atmospheres, has been demonstrated. Contributions to lignite reactivity were found to be similar for calcium and sodium when the cation concentration was expressed on a mole/g fixed carbon basis. Addition of controllable amounts of these ions was found to be practical in a lab scale operation.

Cation-enriched char gasification reactivity in steam atmospheres was correlated with lignite, sodium and calcium concentrations. The resulting correlation provided adequate first approximations of ROM carbon conversion. However, no similar relationship was obtained for chars gasified in steam/air atmospheres. Future studies will elucidate the possible rate controlling mechanisms of steam/air lignite gasification at several pressures.

The method of char reactivity analysis based on the dimensionless time parameter, τ, has been shown to be a convenient and accurate method of predicting char gasification behavior in various reactant atmospheres. The relative ease of half-time measurements, compared with more elaborate carbon conversion-time analyses facilitates the design and interpretation of lab scale gasification studies to evaluate the suitability of coals to various gasification processes.

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APPENDIX A. Sample Calculation for the Prediction of Steam/Air Gasification Behaviour from the Experimental Determination of $t_{1/2}$ in Steam-Only Atmospheres

APPENDIX A. Sample Calculation for the Prediction of Steam/Air Gasification Behaviour from the Experimental Determination of $t_{1/2}$ in Steam-Only Atmospheres

Example Run C3

1. Determination of the extent of carbon conversion due to steam:

The reaction

$$C + H_2O \rightleftharpoons CO + H_2 \qquad (15)$$

proceeds according to first order kinetics. Thus the apparent rate constant, k', can be estimated from the experimental determination of $t_{1/2}$ of Coronach char in steam at 800°C and 2 MPa (i.e., Run C5) and the first order rate expression in terms of the half-time is (2):

$$k' = \frac{\ln(2)}{t_{1/2}} \qquad (16)$$

The half time value is obtained from Table 8 and k' is calculated as 0.0111 min^{-1}. However, the amount of coal charred and subsequently gasified was 125 g in steam-only atmospheres compared to 250 g in air/steam char gasification runs. This calculated value of k' is divided by 2 in order to account for the larger quantity of coal used in Run C3 compared with Run C5. The extent of carbon conversion due to steam can then be determined from (17):

$$X = 1 - e^{-k't} \qquad (17)$$

where k' = .00555 min^{-1} and the results are presented in Table 10.

2. Determination of the extent of carbon conversion due to oxygen.

The reaction

$$C + O_2 \rightleftharpoons CO_2 \qquad (18)$$

proceeds instantaneously at the conditions present inside the reactor. The flowrate of air to the gasifier was maintained constant for all steam/air gasification experiments at 0.212 moles/min (0.0445 moles O_2/min).

From the stoichiometry of reaction (18) the amount of carbon converted due to oxygen can be evaluated. The fractional carbon conversion can be calculated from (19):

$$X_{O2} = \frac{(0.0445 \text{ mole C/min})(12 \text{ g C/mole})}{M_{ci}} \times \text{time} \qquad (19)$$

where M_{ci} = mass of carbon present in char at the start of gasification. The results are presented in Table 10.

3. Determination of the extent of reaction due to the Boudard reaction.

The Boudard reaction (20)

$$C + CO_2 \rightleftharpoons 2CO \qquad (20)$$

proceeds to an extent determined by the equilibrium conditions at the reactor exit.

The equilibrium constant expressed in terms of the partial pressures of CO and CO_2 is (21):

$$K_{eq} = \frac{P^2_{co}}{P_{co_2}} \tag{21}$$

and when expressed in the number of moles of each species becomes (22):

$$K_{eq} = \frac{P_{tot} \times N^2_{co}}{N_{tot} \times N_{co_2}} \tag{22}$$

where P_{tot} is the total pressure and N_{tot} is the total number of moles.

Based on the assumption that the steam-carbon reaction proceeds independently from reactions (15) and (20) the molar quantities of CO and CO_2 can be related to the input oxygen feed to the reactor (23):

$$N_{o_2} = 1/2N_{co} + N_{co_2} \tag{23}$$

and the total number of moles in the system can be expressed as (24):

$$N_{tot} = N_{co} + N_{co_2} + N_{air} \tag{24}$$

Equations (22), (23) and (24) can be solved simultaneously with the following known quantities:

$$N_{o_2} = 0.0445 \text{ g mole/min}$$

$$P_{tot} = 2 \text{ MPa}$$

$$N_{air} = 0.212 \text{ g mole/min}$$

$$K_{eq} = 9.09 \text{ MPa}$$

Substitution and rearrangement of equations (21), (22) and (23) results in the following quadratic equation (25):

$$2.136\ N^2_{co} + 0.482\ N_{co} - .0518 = 0 \qquad (25)$$

Solving by trial and error

$$N_{co} = .0793 \text{ g mole/min}$$

and the extent of carbon conversion can be determined from the stoichiometry of the Boudard reaction or

$$X_{Boud} = \frac{.0.0793/2 \text{ X } 129/\text{g mole}}{M_{ci}} \text{ x } t = \frac{0.4758t}{M_{ci}}$$

where M_{ci} = mass of carbon in char at the start of gasification.

The results are presented in Table 10.

Table 10. CARBON CONVERSION DUE TO STEAM, OXYGEN AND CARBON DIOXIDE

Time (min)	X_{STEAM}	X_{O_2}	X_{BOUD}	X_{TOT}
5	.0274	.0193	.017	.0639
10	.0540	.0387	.0345	.1272
15	.0800	.0580	.0517	.1897
20	.1051	.0774	.0690	.2515
25	.1296	.0967	.0862	.3125
30	.1534	.1161	.1034	.3729
35	.1766	.1354	.1207	.4327
40	.1991	.1548	.1379	.4918
45	.2210	.1141	.1552	.5503
50	.2423	.1741	.1724	.6082
60	.2832	.2322	.2069	.7223
70	.3219	.2709	.2413	.8341
80	.3585	.3096	.2758	.9439

POOR

QUALITY

ORIGINAL